Amendment Under 37 C.F.R. § 1.111
Appln. No.: 09/980,010

REMARKS

Claims 1, 3, 4, 6-9 and 12-17 are all the claims pending in the application. The Examiner included claim 11 in the rejections, however, claim 11 was earlier canceled. Support for the changes to independent claims 1 and 12 may be found in the specification as originally filed, for example, at page 7, lines 10-19, Examples 1 to 12, and page 8, lines 7-8. Support for new claims 14-17 may be found in the specification as originally filed, for example, in the Examples and at page 4, line 21-page 5, line 12.

I. Statement of Substance of Interview

Applicants wish to thank Examiner Bissett and Examiner Sergent for the helpful and courteous interview conducted on December 17, 2003. The "Interview Summary" accurately memorialized the general discussion. During the interview, the rejections of the Office Action dated August 13, 2003 were discussed and the Examiner's positions concerning the scope of the language of the pending claims were discussed.

II. The Objection to the Disclosure

The Examiner acknowledges Applicants' amendments to the specification, but states that the changes "[do] not correct all of the grammatical and typographical errors present in the rest of the specification."

File herewith is a substitute specification. Applicants respectfully submit that Applicants' substitute specification is clear, definite and in proper idiomatic English and it is requested that the objection to the specification be reconsidered and withdrawn. If the Examiner becomes aware of any further changes required to clarify the grammar in the specification, she is requested to point out the changes required so that corrections may be made.

The required statement that the substitute specification contains no new matter is set forth below.

For the above reasons, it is respectfully submitted that Applicant's specification fully complies with 35 U.S.C. § 112, 37 C.F.R. § 1.71 and MPEP §608.01 and it is requested that the objection to the specification be reconsidered and withdrawn.

III.   Statement Concerning the Substitute Specification

The undersigned hereby states that the herein attached Substitute Specification contains no new matter, that the herein attached marked up copy of the substitute specification shows the matter being added to and the matter being deleted from the specification of record and that the Substitute Specification contains the same changes that are indicated in the herein attached marked up copy.

IV.   Paragraphs 7-24 - The Art Rejections

In the Office Action dated August 13, 2003, the Examiner maintained each of the following art rejections:

Claims 1, 9, and 12-13 are rejected under 35 U.S.C. §102(b) as allegedly being anticipated by Ormsby et al as evidenced by Bright.

Claims 1, 3-4, 9, and 12-13 are rejected under 35 U.S.C. §103(a) as allegedly being unpatentable over Okoroafor et al in view of Ormsby et al as evidenced by Bright.

Claims 7 and 8 are rejected under 35 U.S.C. §103(a) as allegedly being unpatentable over Ormsby et al as evidenced by Bright and further in view of Perrott et al.

Claim 6 is rejected under 35 U.S.C. §103(a) as allegedly being unpatentable over Ormsby et al as evidenced by Bright and further in view of Toba et al.

The Examiner states that the §132 Declaration filed June 9, 2003 is insufficient to overcome the rejections based upon Okoroafor et al or Ormsby et al because "the scope of the structures the applicant claims overlap the structures found in the references."

The Examiner also states that Applicants appear "to be depending on elements not found in the claims to differentiate the claims from the prior art."

As discussed during the interview, the Examiner's position was that Applicants' claims did not exclude a second curing agent, such as trimethylol

propane in addition to the curing agent listed in Applicants' claims. That is, the Examiner alleged that Applicants' claims read on, and that Ormsby disclosed, a cured polyurethane mixture of a polyurethane prepolymer with an isocyanate group on both ends obtained from a mixture consisting of diisocyanate and polyol, a curing agent consisting of a polyurethane polyol with a hydroxyl group on at least both ends obtained from diisocyanate and polyol, and a photochromic organic compound, and a trimethylol propane. Concerning Ormsby, it also appeared to be the Examiner's position that Ormsby disclosed reactants that could be Applicants' claimed polyurethane prepolymer and a polyurethane polyol with a hydroxyl group on at least both ends obtained from diisocyanate and polyol.

Concerning Okoroafor, using a similar analysis, the Examiner's position was not that the thiourethane was within the scope of Applicants' claimed "mixture of a polyurethane prepolymer with an isocyanate group on both ends obtained from diisocyanate and polyol". (This appeared to be a change from Examiner Rebar's position). Rather, it appeared to be the Examiner's position that Applicants' claims did not exclude a thio reactant in addition to the mixture of a polyurethane prepolymer with an isocyanate group on both ends obtained from a mixture consisting of diisocyanate and polyol, a curing agent consisting of a polyurethane polyol with a hydroxyl group on at least both ends obtained from diisocyanate and polyol, and a photochromic organic compound. The Examiner particularly noted Okoroafor, column 5, line 55+ and column 8, line 37+.

Applicants respectfully submit that the present invention is not anticipated

by or obvious over the disclosures of Ormsby et al, alone or in view of the secondary

references, or over the disclosures of Okoroafor et al in view of Ormsby et al, and

request that the Examiner reconsider and withdraw these rejections in view of the

following remarks.

First of all, Applicants have amended the independent claims to further

define and clarify the components of the photochromic layer and the cured

polyurethane reaction product.   The cured polyurethane reaction product is

obtained from a mixture consisting essentially of a polyurethane prepolymer with

an isocyanate group on both ends obtained from a mixture consisting of

diisocyanate and polyol, a curing agent consisting of a polyurethane polyol with a

hydroxyl group on at least both ends obtained from diisocyanate and polyol, and a

photochromic organic compound, adhering to each of said two transparent synthetic

resin sheet layers.   The transitional phrase "consisting essentially of" excludes

unlisted ingredients that "materially affect the basic and novel properties of the

invention." The transitional phrase "consisting of" excludes unlisted ingredients.

Applicants respectfully submit that the claimed components do not contain

the components of the systems of the cited art.

Applicants also submit the following comments on the disclosures of the cited

art. The Examiner states that Applicants argue that "the crosslinking agents in

Ormsby et al are only catalysts (Office Action, page 7, paragraph 19). Applicants

respectfully submit that the Examiner has misunderstood Applicants' argument.

As stated in the Amendment dated June 3, 2003, page 9, paragraph IV , line 10,

"[i]n Ormsby et al, tri-methylol propane functions as the curing agent". Also in the

Amendment, page 11, lines 2 to 3, there is the statement "using the tri-methylol

propane of Ormsby et al as the curing agent". That is, the trimethylol propane is

not a catalyst, but it is a curing agent.

The Examiner also used the term "a triol" to describe the curing agents of

Ormsby et al. However, Ormsby et al does not discloses a broad range of curing

agents, such as triols in general. Rather, the curing agent of Ormsby et al is limited

to trimethylol propane (Ormsby et al, col. 3, line 42, col., 4, line 26 and claim, 6).

The Examiner "shows" the polymer in Ormsby et al using a diagram on

page 6 of the Office Action, stating "the structure also meets the applicant's defined

structure in claim 1, where the polyurethane prepolymer are represented ... by

rectangle-hexagon-rectangle sequences, and the curing agent is represented by the

triangle-rectangle-triangle sequence." The diagram may be representative of the

polymer in Ormsby et al. However, said diagram is not a correct representation of

the cured polyurethane of the present invention. The curing agent of the present

invention is a polyurethane polyol with a hydroxyl group on at least both ends

obtained from diisocyanate and polyol. Therefore, the curing agent of the present

invention does not have a structure such as that represented by the triangle-

rectangle-triangle sequence. This triangle-rectangle-triangle sequence does not

contain a structure of a polyurethane polyol with a hydroxyl group on at least both

ends, as in the present invention.

Regarding the Examiner's definition of the term polycarbonate, Applicants

respectfully submit that a "polycarbonate" is a term in the art that defines a class of

polymers. The definition of the term polycarbonate is a polyester derived from a

reaction of carbonic acid derivatives with diols and has the formula:

$$R'-[(O(CO)OR)]_n-OH$$

See the attached definition of a polycarbonate from Kirk-Othmer Encyclopedia of

Chemical Technology, Vol. 18, 3rd Ed., page 479.

The structure of poly (allyldiglycol) carbonate is shown in "Chemical Survey"

No. 39, 1998, p174-175 (English translation).

Regarding the Examiner's statements concerning the definition of the term

"photochromism" (page 7, paragraph 18 of the office action), Applicants respectfully

submit that Applicants' statements concerning "photochromism" in the Amendment

dated June 3, 2003 are within the commonly understood meaning of

photochromism. Regarding the definition of term "photochromism", Applicants

submit herewith three Japanese publications and the partial English translation

thereof. The term "photochromism" is defined in the three publications as follows:

Photochromism means the phenomena that a substance species changes its

color in the state of a solid or a solution by irradiation of a light (an ultraviolet light

or visible rays) and again reverts to its original color in a dark place (generally the reverting speed is low) (Physical and Chemical Dictionary, Iwanami)).

Photochromism is defined as reversible change (A ↔ B) of a single compound which is caused due to a photoelectromagnetic wave in at least one process between two states having different absorption spectrum to each other (Experimental Chemical Lecture No.12, fourth edition).

UV

A   ↔   B

Vis

colorless form   colored form
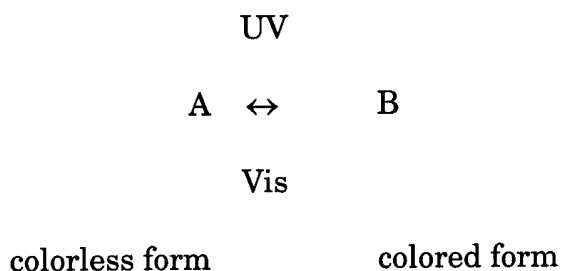
As described in the above formula, photochromism is defined as "the phenomena that a single chemical species reversibly isomerizes between two states different in absorption spectrum to each other without changing its molecular weight by action of a light (Chemical Survey, (quarterly publication), No. 28).

Each definition of photochromism described in the three publications has the same meaning. A person of ordinary skill in the art readily understand that the term "photochromism" has the above-discussed meaning. Also in the present specification, it is clear that the term "photochromism" is used in its art recognized

sense, and has the above-discussed meaning. The laminate of the present invention

has a photochromic layer comprising a photochromic organic compound.

The present specification describes on page 3, line 3, to page 4, line 2, that

"[a]n object of the present invention is to provide a transparent synthetic resin

laminate with photochromism property in which both a color development speed

and a color disappearance speed are high ...." That is, the photochromism property

of the present invention is evaluated and measured as a color development speed

and a color disappearance speed. The method for measurement of color

development speed and color disappearance speed is described in Applicants'

specification, page 19, line 3, to page 4, line 14.

Color is expressed as transmittance. The method for measurement of

transmittance is described in Applicants' specification, page 18, lines 1 to 9. An

ultraviolet light is applied as a light for irradiation. The non-irradiation of

ultraviolet light is a dark state. The change of transmittance, i.e., a change of color

between non-irradiation of ultraviolet light and irradiation of ultraviolet light

signals a reversible change (A ↔ B) of a photochromic compound. That is, this

means photochromism is exhibited. Color development speed (ta) and color

disappearance speed (tb) are described on page 20, lines 5 to 11.

Physical and Chemical Dictionary (Iwanami) describes that the reverting

speed to original color in a dark place is low.

Each ta and tb are measured as a time in which transmittance is changed from T1 or T2 to (T1+T2)/2. Herein, (T1+T2)/2 shows half value period of transmittance.

In Chemical Survey (quarterly) No.28, the life of the colored species with photochromism is determined as its half value period ($\tau_{1/2}$, min) of transmittance (page 53, paragraph 1.2, lines 7 to 9 and page 55, Figure 3).

In Experimental Chemical Lecture No. 12, as a method for evaluation of photochromic characteristics, a method comprising determining half value period in the degree of coloration due to a light has been often applied. Further, the publication describes on page 191, lines 5 to 6 that each sensitivity of color development and color disappearance depends on quantum yield (φ) X absorption coefficient (ξ).

Thus, both the photochromism property and the method for evaluation of the photochromism property as in the present invention are based on the common knowledge of a person of ordinary skill in the art.

If the Examiner maintains the position that Applicants use of the term "photochromism" in the present invention is different than that known in the art, the Examiner is requested to particularly explain the position that Applicants' statements conflict with the commonly understood meaning of photochromism.

The Examiner further states that Applicants have not shown that bending a laminate structure to form a lens imparts to the lens any properties that would make it patentably distinct from the molded lens in Ormsby. Submitted herewith is a Declaration Under 37 C.F.R. § 1.132, including comparative experiments which demonstrate that it is far more difficult to form a lens by bending the transparent synthetic resin laminate using the curing agent (tri-methylol propane) as disclosed in Ormsby et al than in the case of the transparent synthetic resin laminate of the present invention.

As shown in the Declaration, when the transparent synthetic resin laminate used the curing agent disclosed in Ormsby et al was employed in the formation of a lens, leakage of the photochromic layer from each discs as a lens occurred due to peeling-off of the photochromic layer from the polycarbonate films as outer layers, so that lenses could not be formed.

Further to the §103 rejections and regarding the Examiner's statements of page 8, paragraph 21, of the Office Action that the polymerizable organic composition of Okoroafor contains both at least one capped polyisocyanate and at least one polythiol as indispensable components and decapped polyisocyanate, polyol and polythiol react to form a polyurethane prepolymer (probably polythiourethane prepolymer). The claims of the present invention, as amended, recite a polyurethane prepolymer obtained from a mixture consisting of

diisocyanate and polyol. Therefore, the use of polythiol is precluded in the production of the polyurethane prepolymer of the present invention.

Regarding pages 8 to 9, paragraph 22, of the Office Action, the capped polyisocyanate in Okoroafor is converted to decapped polyisocyanate and nonfugitive capping groups (Okoroafor, col. 3, lines 1 to 5) and nonfugitive capping groups react with other nonfugitive capping groups to from oligomeric species or react with decapped isocyanate or reactive hydrogen groups to form polymeric species (Okoroafor, col. 3, lines 13 to 21). The claims of the present invention recite a polyurethane prepolymer obtained from a mixture consisting of diisocyanate and polyol. Therefore, formation of such oligomeric species or such polymeric species is precluded in the production of the polyurethane prepolymer of the present invention.

As to the Examiner's statement that "[t]his negative effect may be overcome by adding ... polyurethane" (Office Action, page 9, lines6 to 9), Applicants respectfully submit that there is no such description in Okoroafor et al. It is questionable whether such negative effect can be overcome by such a treatment as raised by the Examiner. That is, when more photochromic compound is added, deactivated photochromic compound may exert any influence on photochromic properties of other activated photochromic compound, and it becomes difficult to adjust suitable amount of photochromic compound and problems of cost may be created. When the photochromic compound is added at some other point it is

difficult to determine the timing of addition without impairing photochromic properties.

Regarding page 9, paragraph 23, of the Office Action, Applicants note that known hindered amine light stabilizers (HALS) and known antioxidants also can be applied to the photochromic layer of the present invention.

Regarding page 9, paragraph 24, of the Office Action, the Examiner appears to state that TDI is used in the production of a polyurethane prepolymer. Applicants respectfully submit that that there is no description in Toba et al that known TDI is used as part of a curing agent. Further, Applicants' claim 6 recites a preferable curing agent.

Even if the cited references are combined, it is respectfully submitted that the present invention would not have been arrived at.

For the above reasons, it is respectfully submitted that the subject matter of claims 1, 3, 4, 6-9, 12 and 13 is neither taught by nor made obvious from the disclosures of the disclosures of Ormsby et al, alone or in view of the secondary references, or over the disclosures of Okoroafor et al in view of Ormsby et al, and it is requested that the rejections under 35 U.S.C. §§102 and 103 be reconsidered and withdrawn.

V.   **Conclusion**

In view of the above, Applicants respectfully submit that their claimed invention is allowable and ask that objection to the specification, the rejection under 35 U.S.C. §102 and the rejections under 35 U.S.C. §103 be reconsidered and withdrawn. Applicants respectfully submit that this case is in condition for allowance and allowance is respectfully solicited.

If any points remain at issue which the Examiner feels may be best resolved through a personal or telephone interview, the Examiner is kindly requested to contact the undersigned at the local exchange number listed below.

Applicants hereby petition for any extension of time which may be required to maintain the pendency of this case.
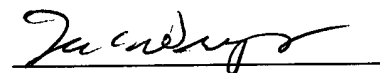
Respectfully submitted,

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Substitute Specification

TRANSPARENT SYNTHETIC RESIN LAMINATE WITH PHOTOCHROMISM PROPERTY

FIELD OF ART

The present invention relates to a transparent synthetic resin laminate with photochromism property and, specifically, to a transparent synthetic resin laminate with excellent photochromism property exhibiting both a high color development speed and a high color disappearance speed. The transparent synthetic laminate may be used as an optical lens and is excellent in both control of thickness of a photochromic coated film and surface smoothness thereof.

BACKGROUND OF THE INVENTION

As conventional optical lenses, such as photochromic lenses, inorganic lenses have generally been used. Usually an inorganic coating layer with photochromic property is added to a surface of a glass or a surface of plastic lenses, such as CR-39. Recently, as a lens itself, the use of plastic lenses with high impact resistance has spread. Particularly, in United States of America, lenses made from a polycarbonate have widely proliferated and demand for sun glasses with impact resistance has rapidly increased because of extensive outdoor activities.

Synthetic resin laminates with photochromism property have hitherto been obtained by adding a photochromic organic compound to a silicone surface curing

coating agent, coating it on one side of a substrate, and then performing cure, and by adding a photochromic organic compound to an urethane coating agent, coating it on one side of a synthetic resin laminate, and then performing cure. (Japanese Patent Kokai (Laid-open) No.63-178193).

However, in the process for coating a coating agent containing a photochromic organic compound on one side of a synthetic resin substrate, it is difficult to obtain a smooth coated film surface and to control a thickness of a coated film. When a coated film surface is not smooth, it is not practical or preferred for use since the laminate as a photochromic lens causes distortion through the lens.

Further, Japanese Patent Kokai (Laid-open) No.61—148048 discloses a photochromic laminate with a photochromic layer containing a spironaphtho oxazine derivative interposed between transparent material layers. Although the prior art discloses an example in which one liquid type polyurethane resin is contained in a photochromic layer, both a color development speed and a color disappearance speed are low, and thus that photochromic laminate is insufficient.

Moreover, also in photochromic lenses, various processes such as direct kneading into a resin and coating on a resin surface have been tried. However, they are not successful and are not put into practice because of performance problems due to insufficient heat resistance of the photochromic elements during kneading, and also due to problems in surface coating, and contrast shortage from limitation of coated film thickness.

Thus, in the present situation, there exists no transparent synthetic resin laminate with photochromism property as a photochromic lens in which both a color development speed and a color disappearance speed are high and surface smoothness of a coated film and control of coated film thickness in a photochromic layer are excellent.

DISCLOSURE OF THE INVENTION

The present invention solves the above-mentioned problems in the prior art. An object of the present invention is to provide a transparent synthetic resin laminate with photochromism property in which both a color development speed and a color disappearance speed are high, contrast in color development is maintained for a long time and the surface smoothness of a coated film and the control of thickness of a coated film in a photochromic layer are excellent.

As a result of studies of the above-mentioned problems in the prior art, the inventors have invented a transparent synthetic resin laminate in which both a color development speed and a color disappearance speed are high and contrast in color development is maintained for a long time and the surface smoothness of a coated film and the control of thickness of a coated film in a photochromic layer are excellent, by interposing a photochromic layer formed by curing a mixture of a two-liquid type polyurethane of a polyurethane prepolymer and a curing agent, and a

3

photochromic organic compound. Optionally, a light stabilizer and an antioxidant between two transparent synthetic resin layers may be used.

That is, the present invention provides a transparent synthetic resin laminate with photochromism property consisting essentially of two transparent synthetic resin layers and a photochromic layer formed by curing a mixture of a two liquid polyurethane of a polyurethane prepolymer and a curing agent, a photochromic organic compound, a light stabilizer and an antioxidant between two transparent synthetic resin layers.

Further, the present invention provides a process for producing a transparent synthetic resin laminate with photochromism property which comprises:

coating a mixture of a two-liquid polyurethane of a polyurethane prepolymer and a curing agent, a photochromic organic compound and a solvent, a light stabilizer, and an antioxidant on one side of a transparent synthetic resin sheet,

then, removing substantially all the solvent from the mixture,

then, adhering another transparent synthetic resin sheet to the coated side of said synthetic resin sheet, and

then, curing the two-liquid polyurethane,

thereby, forming a photochromic layer.

The present invention will be described in detail below.

4

The transparent synthetic resin to be used in the present invention is not limited as long as it is a resin with high transparency. It is preferable to use a polycarbonate resin and a polymethylmethacrylate resin. As the combination of two transparent synthetic resins, a polycarbonate resin, a polymethylmethacrylate or both thereof is (are) applied to the two transparent synthetic resins. A transparent synthetic resin with a thickness of 50 to 2000 μm may be used. When bending into a lens form is performed, it is preferable to use a synthetic resin sheet with a thickness of 100 to 1000 μm.

The present invention relates to a photochromic layer formed by cure of a two-liquid polyurethane of a polyurethane prepolymer and a curing agent containing a photochromic organic compound, a light stabilizer, and an antioxidant between two transparent synthetic resin layers. Thereby, it becomes possible to produce industrially a transparent synthetic resin laminate excellent in both heat resinstance and impact resistance that exhibits a high color development speed and a high color disappearance speed in use as a lens and possesses photochromic performance that is excellent in surface smoothness of a coated film in a photochromic layer, equivalent to conventional inorganic types, and maintains a photochromic characteristics, such as contrast in color development, for a long period of time.

Generally, polyurethane includes one-liquid type and two-liquid type. In the present invention, it is preferable from the aspects of color development speed, color

disappearance speed, and solubility of photochromic compound and various additives to use a two liquid polyurethane of a polyurethane prepolymer and a curing agent. Actually, a prepolymer is dissolved in a specific solvent and mixed with various additives including a photochromic compound and then a curing agent is added thereto.

As the polyurethane prepolymer, a compound obtained by reaction of isocyanate and polyol in a specific proportion is used. That is, the polyurethane prepolymer is a compound with an isocyanate group on both ends obtained from diisocyanate and polyol. The diisocyanate compound to be used for the polyurethane prepolymer is preferably diphenylmethane-4,4'-diisocyanate (MDI). Further, as the polyol, it is preferable to use polypropylene glycol (PPG) with a polymerization degree of 5 to 30.

The molecular weight of the polyurethane prepolymer is a number average molecular weight of 500 to 5000 and preferably 1500 to 4000 and more preferably 2000 to 3000.

The curing agent is not limited as long as it is a compound with two hydroxyl groups. Examples of the curing agent include polyurethane polyol, polyether polyol, polyester polyol, acryl polyol, polybutadiene polyol and polycarbonate polyol, among which polyurethane polyol with a hydroxyl group on its end, obtained from specific isocyanate and specific polyol, is preferable. Particularly, polyurethane polyol with a hydroxy group on at least both ends derived from diisocyante and polyol is

6

preferable and it is preferable to use tolylenediisocyanate (TDI) as the diisocyanate. Further, as the polyol, it is preferable to use PPG with polymerization degree of 5 to 30.

The molecular weight of the curing agent is a number average molecular weight of 500 to 5000 and preferably 1500 to 4000 and more preferably 2000 to 3000.

In order to adjust the viscosity of the polyurethane prepolymer and the curing agent, a solvent such as ethyl acetate and tetrahydrofurane may be used.

In the present invention, the organic compound with photochromic property is not limited as long as it has good compatibility with the polyurethane prepolymer. Photochromic organic compound obtainable on the market can be used. From the aspect of photochromic performance spiropyran compounds, spiroxazine compounds, and naphthopyran compounds are preferably used as the photochromic organic compound.

Examples of the spiropyran compound include 1',3',3'-trimethylspiro(2H-1-benzopyran-2,2'-indoline), 1',3',3'-trimethylspiro-8-nitro(2H-1-benzopyran-2,2'-indoline), 1',3',3'-trimethyl-6-hydroxyspiro(2H-1-benzopyran-2,2'-indoline), 1',3',3'-trimethylspiro-8-methoxy(2H-1-benzopyran-2,2'-indoline), 5'-chloro-1',3',3'-trimethyl-6-nitrospiro(2H-1-benzopyran-2,2'-indoline), 6,8-dibromo-1',3',3'-trimethylspiro(2H-1-benzopyran-2,2'-indoline), 8-ethoxy-1',3',3',4',7'-pentamethylspiro(2H-1-benzopyran-2,2'-indoline), 5'-chloro-1',3',3'-trimethylspiro-6,8-dinitro(2H-1-

7

benzopyran-2,2'-indoline), 3,3,1-diphenyl-3H-naphtho(2,1-b) pyran, 1,3,3-triphenylspiro[indoline-2,3'-(3H)-naphtho(2,1-b)pyran], 1-(2,3,4,5,6-pentamethylbenzyl)-3,3-dimethylspiro[indoline-2,3'-(3H)-naphtho(2,1-b)pyran], 1-(2-methoxy-5-nitrobenzyl)-3,3-dimethylspiro[indoline-2,3'-naphtho(2,1-b)pyran], 1-(2-nitrobenzyl)-3,3-dimethylspiro[indoline-2,3'-naphtho(2,1-b)pyran], 1-(2-naphthylmethyl)-3,3-dimethylspiro[indoline-2,3'-naphtho(2,1-b)pyran] and 1,3,3-trimethyl-6'-nitro-spiro[2H-1-benzopyran-2,2'-[2H]-indole].

Examples of the spiroxazine compound include 1,3,3-trimethylspiro [indolino-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 5-methoxy-1,3,3-trimethylspiro [indolino-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 5-chloro-1,3,3-trimethylspiro [indolino-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 4,7-diethoxy-1,3,3-trimethylspiro [indolino-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 5-chloro-1-butyl-3,3-dimethylspiro [indolino-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 1,3,3,5-tetramethyl-9'-ethoxyspiro [indolino-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 1-benzyl-3,3-dimethylspiro [indoline-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 1-(4-methoxybenzyl)-3,3-dimethylspiro [indoline-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 1-(2-methylbenzyl)-3,3-dimethylspiro [indoline-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 1-(3,5-dimethylbenzyl)-3,3-dimethylspiro [indoline-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 1- (4-chlorobenzyl)-3,3-dimethylspiro [indoline-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 1-(4-bromobenzyl)-3,3-dimethylspiro [indoline-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 1-(2-fluorobenzyl)-3,3-dimethylspiro [indoline-2,3'-[3H] naphtho[2,1-b] [1,4] oxazine], 1,3,5,6-tetramethyl-3-ethylspiro [indoline-2,3'-[3H] pyrido [3,2-f] [1,4]-benzoxazine],

8

1,3,3,5,6-pentamethylspiro [indoline-2,3'-[3H] pyrido [3,2-f] [1,4]-benzoxazine], 6'-(2,3-dihydro-1H-indole-1-yl)-1,3-dihydro-3,3-dimethyl-1-propyl-spiro [2H-indole-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 6'-(2,3-dihydro-1H-indole-1-yl)-1,3-dihydro-3,3-dimethyl-1-(2-methylpropyl)-spiro [2H-indole-2,3'-[3H]-naphtho [2,1-b] [1,4]oxazine], 1,3,3-trimethyl-1-6'-(2,3-dihydro-1H-indole-1-yl)-spiro [2H-indole-2,3'-[3H]-naphtho [2,1-b] [1,4] oxazine], 1,3,3-trimethyl-6'-(1-piperidinyl)-spiro [2H-indole-2,3'-[3H]-naphtho [2, 1-b] [1,4] oxazine], 1,3,3-trimethyl-6'-(1-piperidinyl)-spiro [2H-indole-2,3'-[3H]-naphtho[2,1-b] [1,4] oxazine], 1,3,3-trimethyl-6'-(1-piperidinyl)-6-(trifluoromethyl)-spiro [2H-indole-2,3'-[3H]-naphtho [2,1-b] [1,4] oxazine] and 1,3,3,5,6-pentamethyl-spiro [2H-indole-2,3'-[3H]-naphtho [2,1-b] [1,4] oxazine].

Examples of the naphthopyran compound include 3,3-diphenyl-3H-naphtho [2,1-b] pyran, 2,2-diphenyl-2H-naphtho [1,2-b] pyran, 3-(2-fluorophenyl)-3-(4-methoxyphenyl)-3H-naphtho [2, 1-b] pyran, 3-(2-methyl-4-methoxyphenyl)-3-(4-ethoxyphenyl)-3H-naphtho [2, 1-b] pyran, 3-(2-furil)-3-(2-fluorophenyl)-3H-naphtho [2,1-b] pyran, 3-(2-thienyl) -3-(2-fluoro-4-methoxyphenyl)-3H-naphtho [2,1-b] pyran, 3-{2-(1-methylpyrrolidinyl)}-3-(2-methyl-4-methoxyphenyl)-3H-naphtho [2,1-b] pyran, spiro (bicyclo [3.3.1] nonane-9,3'-3H-naphtho [2,1-b] pyran), spiro (bicyclo [3.3.1] nonane-9-2'-3H-naphtho [2,1-b] pyran), 4-[4-[6-(4-morpholinyl)-3-phenyl-3H-naphtho [2,1-b] pyran-3-yl] phenyl]-morpholine, 4-[3-(4-methoxyphenyl)-3-phenyl-3H-naphtho [2, 1-b] pyran-6-yl]-morpholine, 4-[3,3-bis(4-methoxyphenyl)-3H-

naphtho [2,1-b] pyran-6-yl]-morpholine, 4-[3-phenyl-3-[4-(1-piperidinyl) phenyl]-3H-naphtho [2, 1-b] pyran-6-yl]-morpholine and 2,2-diphenyl-2H-naphtho [2,1-b] pyran.

In order to ensure the life of the synthetic resin laminate of the present invention, it is necessary to add various stabilizers. As the stabilizer, light stabilizers, such as hindered amines and antioxidants such as hindered phenols are added.

Examples of the hindered amine include bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidinyl)-[[3,5-bis(1,1-dimethylethyl)]-[4-hydroxyphenyl]methyl]butyl malonate, 1-(methyl)-8-(1,2,2,6,6-pentamethyl-4-piperidinyl)-sebacate, 1-[2-(3-(3,5-di-t-butyl-4-hydroxyphenyl) propionyloxy)ethyl]-4-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy]-2,2,6,6-tetramethylpiperidine, 4-benzoyloxy-2,2,6,6-tetramethylpiperidine, triethylene-diamine and 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4,5]decane-2,4-dione. As other nickel ultraviolet ray stabilizer, [2,2'-thiobis(4-t-octylphenolate)]-n-butylamine nickel, nickel complex-3,5-di-t-butyl-4-hydroxybenzyl·phsosphoric acid monoethylate and nickel·dibutyl carbamate also can be used. A tertiary hindered amine compound is preferable. Particularly, a hindered amine light stabilizer of bis(1,2,2,6,6-pentamethyl-4-piperidinyl)-sebacate or a condensation product of 1,2,2,6,6-pentamethyl-4-piperidinol, tridodecyl alcohol, and 1,2,3,4-butanetetra caboxylic acid, is preferable.

Examples of the antioxidant include 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl) butane, 2,2'-methylenebis (4-ethyl-6-t-butylphenol), tetrakis-[methylene-3-(3',5'-di-t-butyl-4'-hydroxyphenyl) propionate]methane, 2,6-di-t-butyl-p-cresol, 4,4'-butylidenebis(3-methyl-6-t-butylphenol), 1,3,5-tris(3', 5'-di-t-butyl-4'-hydroxybenzyl)-S-triazine-2,4,6-(1H, 3H, 5H)trione, stearyl-ß-(3,5-di-t-butyl-4-hydorxyphenyl)propionate, 1,3,5-tris(4-t-butyl-3-hydroxy-2,6-dimethylbenzyl) isocyanuric acid, 4,4'-thiobis(3-methyl-6-t-butylphenol) and 1,3,5-trimethyl-2,4,6-tris (3,5-di-t-butyl-4-hydroxybenzyl) benzene.

Particularly, a phenol antioxidant of 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl) butane tetrakis-[methylene-3-(3',5'-di-t-butyl-4'-hydroxyphenyl) propionate] methane and 1,3,5-tris(3,5-di-t-butyl-4-hyroxybenzyl)-1,3,5-triazine-2,4,6-(1H, 3H, 5H)-trione, which contains 3 or more hindered phenols, is preferable.

The transparent synthetic resin laminate with photochromic property of the present invention is produced according to the process below. A photochromic organic compound is added in the proportion of 0.2 to 5 % to resin solid matter in a solution of a polyurethane prepolymer diluted with specific organic solvent and an additive(s) of hindered amine light stabilizer and/or antioxidant is (are) added thereto in the proportion of 0.1 to 5 % to resin solid matter and uniformly mixed with stirring. Then, a curing agent is added thereto in a I/H ratio of isocyanate group (I) to hydroxyl group (H) of 0.9 to 20, and preferably 1 to 10, and stirring is further performed to form a solution. It is suitable that the polymer concentration

in the solution thus obtained is 40 to 90 % by weight. The solution is coated with a doctor blade of coating thickness 100 to 1000 μm on one side of a transparent synthetic resin sheet. After the completion of coating, heat drying is performed to the state substantially not containing the solvent on the coated surface and another transparent synthetic resin sheet is adhered to the coated surface of said synthetic resin sheet in a sandwich form. The above-mentioned heat drying is usually performed at 20 to 50°C for 5 to 60 minutes. A laminate sheet thus obtained is heated to cure the polyurethane prepolymer containing the curing agent, whereby a transparent synthetic resin laminate is obtained. The curing conditions of the polyurethane prepolymer are usually 60 to 140 °C and 2 hours to 1 week.

Examples of the solvent include hydrocarbons such as hexane, heptane, octane, cyclohexane, toluene, xylene and ethyl benzene, esters such as ethyl acetate, methyl acetate, isopropyl acetate, n-propyl acetate, isobutyl acetate, n-butyl acetate, isoamyl acetate, methyl propionate and isobutyl propionate, ketones such as acetone, methylethyl ketone, diethyl ketone, methylisobutyl ketone, acetyl acetone and cyclohexyl ketone, ether esters such as cellosolve aetate, diethylglycol diaetate, ethyleneglycol mono n-butylether acetate, propylene glycol and monomethylether acetate, tertiary alcohols such as diacetone alcohol and t-amyl alcohol and tetrahydofuran. Particularly, ethyl aetate, tetrahydrofuran and toluene are preferable.

12

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention will be described in more detail below, referring to Examples, which are not intended to limit the scope of the present invention.

Examples 1 to 4

2 % of Photochromic compound 1 or 2 per resin solid matter and 1 to 2 % of Additive 1 per resin solid matter were dissolved in a solution of 15 g of a polyurethane precursor having a NCO group equivalent weight (equivalent weight is the average molecular weight per one functional group) of 1500 obtained by reaction of diphenylmethane-4,4'-diisocyanate and polypropylene glycol having an average polymerization degree of 15 diluted with 8.3 g of tetrahydrofuran and stirred until uniformity was ensured and then 3 g of a curing agent having a hydroxyl group equivalent weight of 1050 obtained by reaction of tolylene diisocyanate and polypropylene glycol having an average polymerization degree of 10 was added thereto and further stirred.

The solution thus obtained was coated with a doctor blade of coating thickness 400 μm, manufactured by Yoshimitsu Seiki K.K., in Japan on a polycarbonate film of thickness 700 μm (trade name IUPILON, manufactured by Mitsubishi Gas Chemical Co., Inc.). After the completion of coating, the solvent was vaporized at 45 °C for 10 minutes in a hot air dryer and the polycarbonate film was adhered to make a sheet form and then heat curing was performed at 70 °C for 2

days. Measurements of the transmittance in maximum absorption wave length and the light resistance for the synthetic resin laminate thus obtained were performed and the thickness of the photochromic layer was measured and its appearance was observed. The proportion of each component for the formation of the laminates was shown in Table 1. The evaluation results of the laminates were shown in Table 2.

Photochromic compound 1:

1,3-dihydro-1,3,3,5,6 (1,3,3,4,5) pentamethyl-spiro[2H-indole-2,3-[3H]-naphtho[2,b] [1,4]oxazine]

Photochromic compound 2:

3,3-diphenyl-3H-naphtho [2, 1-b] pyran

Additive 1:

bis (2,2,6,6-tetramethyl-4-piperidinyl) sebacate

Each performance was evaluated according to the following methods.

[Measurement of transmittance]

A single wave length light of 360 nm was irradiated with an ultramonochromatic light source. Transmittance after 5 minutes from the start of the irradiation and transmittance with non-irradiation were measured. A spectrophotometer, manufactured by Nihon Bunko k.k., Japan, was used in the

measurement of transmittance and transmittance in maximum absorption wave length was measured.

[Evaluation of light resistance]

Contrast prior to exposure and contrast after exposure to a sunshine weather meter for 60 hours under the conditions below were measured. In order to compare with contrast prior to exposure, contrast retention percentage was calculated to evaluate its life.

(1) Setting conditions of sunshine weather meter

· Irradiance: 255 w/m^2 (300 to 700 nm)
· Temperature: room temperature
· Rainfall was not applied.

(2) Calculation of contrast retention percentage (%)

Contrast retention percentage (%)
$=(L^*_3 - L^*_4) \times 100/(L^*_1 - L^*_2)$

· L^*_1 : contrast prior to light resistance test
   (in ultraviolet light non-irradiation)
· L^*_2 : contrast prior to light resistance test
   (in ultraviolet light irradiation)
· L^*_3 : contrast after light resistance test

15

(in ultraviolet light non-irradiation)

· L_4^* : contrast after light resistance test

(in ultraviolet light irradiation)

(3) Evaluation

Contrast life was evaluated based on the following criterion.

○ : contrast retention percentage after light

resistance test is 70 % or above.

● : contrast retention percentage after light

resistance test is below 70 %.

[Color development speed and color disappearance speed]

Color development speed (ta) and color disappearance speed (tb) were

measured as below.

T1 : transmittance in non-irradiation of

ultraviolet light

T2 : transmittance in irradiation of ultraviolet

light

ta : a time in which transmittance is changed from

T1 to (T1+T2)/2 by irradiation of ultraviolet

light

tb : a time in which transmittance is changed from

T2 to (T1+T2)/2 by shielding irradiated

ultraviolet light

Both ta and tb were determined by a curve of change of transmittance in maximum absorption wave length with the lapse of time.

Comparative Example 1

The synthetic resin laminate was obtained in the same experiment as in Example 1, except that the urethane was changed to solvent type one-liquid, Hamatai Y-7122-A, manufactured by Yokohama Gomu k.k., Japan. The proportion of each component was shown in Table 1 and the evaluation results were shown in Table 2.

Examples 5 to 12

1 % of Photochromic compound 3 per resin solid matter and 0.5 % of Photochromic compound 4 per resin solid matter were added to a solution of 15 g of a polyurethane precursor diluted with 13.6 g of an organic solvent (toluene 4.6 g, methylethyl ketone 1.8 g and ethyl acetate 7.2 g) in the same manner as in Example 1 and each of the Additives 1 to 4 was further added thereto in the blend proportion shown in Table 3 and dissolved and 1.6 g of the same curing agent as in Example 1 was added thereto and stirred.

The solution thus obtained was coated with a doctor blade of coating thickness 300 μm, manufactured by Yoshimitsu Seiki k.k., Japan, on a

17

polycarbonate film of thickness 300 μm (trade name IUPILON, manufactured by Mitsubishi Gas Chemical Co., Inc.). After the completion of coating, the solvent was vaporized at 45 °C for 10 minutes in a hot air dryer. Another polycarbonate film of 300 μm was adhered thereto to make a sheet form and heat curing was performed at 70 °C for 3 days. The same evaluation as in Example 1 was performed for the synthetic resin laminate thus obtained. In the evaluation of light resistance, the evaluation was performed by changing the apparatus and further increasing ultraviolet light radiant intensity. The evaluation results were shown in Table 4. Further, when the samples thus prepared were exposed to sun light, they turned brown, and when they were put in a dark place, color disappearance occurred.

Organic Photochromic compound 3 :

4-[4-[6-(4-morpholynyl)-3-phenyl-3H-naphtho [2,1-b] pyran-3-yl] phenyl]-morpholine

Organic Photochromic compound 4 :

1,3-dihydro-1,3,3,5,6(1,3,3,4,5)-pentamethyl-spiro(2H-indole-2,3-[3H]-naphtho[2,b] [1,4]oxazine]

Additive 1 : the same as in Example 1

bis (2,2,6, 6—tetramethyl-4-piperidinyl) sebacate

18

Additive 2 :

bis (1,2,2,6, 6-pentamethyl-4-piperidinyl) sebacate

Additive 3 :

bis(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate

1-(methyl)-8-(1,2,2,6,6-pentamethyl-4-piperidinyl)-sebacate

Additive 4 :

1,1,3-tris (2-methyl-4-hydroxy-5-t-butylphenyl) butane

The measurement of transmittance and the measurement and evaluation of color development speed and color disappearance speed were performed in the same manner as in Example 1.

[Evaluation of light resistance]

A UV lamp was irradiated for 5 minutes prior to light resistance test and after light resistance test and then contrast due to color development and color difference were measured and contrast retention percentage and color change degree in color disappearance in the light resistance test were calculated. Thus, light resistance was evaluated. In the light resistance test, an apparatus with a xenon lamp as the light source (apparatus name SUNTEST CPS+, maker :

manufactured by ATLAS) was used and an irradiance of 750 W/m^2 (300 to 800 nm)

for 20 hours was applied. Further, the UV lamp had a single wave length of 360 nm

in an ultramonochromatic light source (Nihon Bunko k.k., Japan)

① Calculation of contrast retention percentage

It was calculated in the same method as in Example 1.

② Calculation of color change degree

color change degree

$$=[(L^*_1 - L^*_3)^2 + (a^*_1 - a^*_3)^2 + (b^*_1 - b^*_3)^2]^{1/2}$$

· a^*_1 : a* value prior to light resistance test
      (ultraviolet light non-irradiation)
· a^*_3 : a* value after light resistance test
      (ultraviolet light non-irradiation)
· b^*_1 : b* value prior to light resistance test
      (ultraviolet light non-irradiation)
· b^*_3 : b* value after light resistance test
      (ultraviolet light non-irradiation)

③ Evaluation

O: After light resistance test, contrast is 70 %
      or above and color change degree is below 5 %.

Δ : After light resistance test, contrast is below
      70 % and color change degree is 5 % or above.

INDUSTRIAL APPLICABILITY

In the formation of a polyurethane layer on a transparent synthetic resin surface, a polyurethane layer could be formed without impairing any photochromic performance by using specific two-liquid thermosetting poyurethane and mixing a polyurethane prepolymer, a curing agent and various additives including a photochromic compound in specific solvent and a transparent synthetic resin laminate with photochromism property to provide high availability could be produced efficiently by ensuring substantially non-solvent state thereof, adhering another transparent synthetic resin, and then performing heat cure. Further, a plastic lens with high photochromic performance and smooth photochromic layer could be obtained readily by using the laminate.

Table 1

	Polyurethane precursor (g)	Curing agent (g)	THF (Note 1) (g)	Species of photochromic compound	Concentration of photochromic compound (g)	Additive	Concentration of additive (%)
Example 1	15	3	8.3	1	2	1	1
2	15	3	8.3	1	2	1	2
3	15	3	8.3	2	2	1	1
4	15	3	8.3	2	2	1	2
Comp.Ex.1	30 (Note 2)	—	—	1	2	1	1

Note 1 : tetrahyrofuran

Note 2 : solvent type one-liquid

22

Table 2

	Thickness of Photochromic layer (µm)	Color in color development	Maximum absorption wave length (nm)	Transmittance in maximum absorption wave length		Color development speed ta (sec)	Color disappearance speed tb (sec)	Appearance	Life
				ulraviolet light in non-irradiation (%)	in irradiation (%)				
Example 1	177	blue	620	83	58	13	13	good	○
2	178	blue	620	83	58	13	13	good	○
3	181	yellow	440	87	65	10	10	good	○
4	179	yellow	440	88	65	10	10	good	○
Comp.Ex.1	175	blue	620	80	52	23	26	good	△

Table 3

	Polyurethane precursor (g)	Curing agent (g)	Toluene MEK (Note 3) ethyl acetae	Photochromic compound species	concentration (%)	Additive — light stabilizer species	concentration (%)	Additive — antioxidant species	concentration (%)
Example 5	15	1.6	13.6	3	1.0	2	3.0	—	—
				4	0.5				
Example 6	15	1.6	13.6	3	1.0	2	3.0	4	3.0
				4	0.5				
Example 7	15	1.6	13.6	3	1.0	3	3.0	—	—
				4	0.5				
Example 8	15	1.6	13.6	3	1.0	3	3.0	4	3.0
				4	0.5				
Example 9	15	1.6	13.6	3	1.0	1	3.0	—	—
				4	0.5				
Example 10	15	1.6	13.6	3	1.0	3	15.0	—	—
				4	0.5				
Example 11	15	1.6	13.6	3	1.0	3	15.0	4	3.0
				4	0.5				
Example 12	15	1.6	13.6	3	1.0	—	—	—	—
				4	0.5				

Note 3 : methylethyl ketone

Table 4

	Thickness of photochromic layer (μm)	Maximum absorption wave length (nm)	Transmittance in maximum absorption wave length ultraviolet light		Color development speed ta (sec)	Color disappearance speed tb (sec)	Appearance	Life		
			in non-irradiation (%)	in irradiation (%)				contrast retention percent (%)	color change degree	Evaluation
Example 5	133	460	84	63	13	15	good	72	3	O
Example 6	140	460	84	65	14	16	good	74	2	O
Example 7	137	460	85	61	14	16	good	70	4	O
Example 8	128	460	84	67	14	16	good	73	3	C
Example 9	136	460	85	65	13	15	good	43	7	△
Example 10	132	460	85	63	14	16	good	51	4	△
Example 11	135	460	84	66	14	16	good	56	3	△
Example 12	138	460	85	67	13	15	good	34	10	△

25

Marked-Up Version of Substitute Specification

TRANSPARENT SYNTHETIC RESIN LAMINATE WITH PHOTOCHROMISM PROPERTY

FIELD OF ART

The present invention relates to a transparent synthetic resin laminate with photochromism property and, specifically, to a transparent synthetic resin laminate with excellent photochromism property exhibiting both a high color development speed and a high color disappearance speed. The transparent synthetic laminate may be used as an optical lens and is excellent in both control of thickness of a photochromic coated film and surface smoothness thereof.

BACKGROUND OF THE INVENTION

As conventional optical lenses, such as photochromic lenses, inorganic lenses have generally been used. ~~That is, u~~Usually[[,]] an inorganic coating layer with photochromic property ~~was~~ is added to a surface of a glass or a surface of plastic lenses, such as CR-39. Recently, as a lens itself, the use of plastic lenses with high impact resistance ~~have~~ has spread. Particularly, in United States of America, lenses made from a polycarbonate have widely proliferated and demand for ~~a~~ sun glasses with impact resistance has rapidly increased because of extensive outdoor activities.

are not successful and are not put into practice because of performance problems due to insufficient heat resistance of the photochromic elements during kneading, and[[,]] also due to problems in surface coating, and contrast shortage from limitation of coated film thickness.

Thus, in the present situation, there exists no transparent synthetic resin laminate with photochromism property as a photochromic lens in which both a color development speed and a color disappearance speed are high and surface smoothness of a coated film and control of coated film thickness in a photochromic layer are excellent.

DISCLOSURE OF THE INVENTION

The present invention solves the above-mentioned problems in the prior art. An object of the present invention is to provide a transparent synthetic resin laminate with photochromism property in which both a color development speed and a color disappearance speed are high, and contrast in color development is maintained for a long time and the surface smoothness of a coated film and the control of thickness of a coated film in a photochromic layer are excellent.

As a result of studies of the above-mentioned problems in the prior art, the inventors have invented a transparent synthetic resin laminate in which both a color development speed and a color disappearance speed are high and contrast in color development is maintained for a long time and the surface smoothness of a

3

As sSynthetic resin laminates with photochromism property[[,]] have hitherto [[,]] been a laminate obtained by adding a photochromic organic compound to a silicone surface curing coating agent, and then coating it on one side of a substrate, and then performing cure, and a laminate obtained by adding a photochromic organic compound to an urethane coating agent, and then coating it on one side of a synthetic resin laminate, and then performing cure. have been known (Japanese Patent Kokai (Laid-open) No.63-178193).

However, in the process for coating a coating agent containing a photochromic organic compound on one side of a synthetic resin substrate, it was is difficult to obtain a smooth coated film surface and to control a thickness of a coated film. Thus, wWhen a coated film surface is not smooth, it is not practically preferable practical or preferred for use since use of the laminate as a photochromic lens causes distortion through the lens.

Further, Japanese Patent Kokai (Laid-open) No.61—148048 discloses a photochromic laminate with a photochromic layer containing a spironaphtho oxazine derivative interposed between transparent material layers. Although the prior art discloses an example in which one liquid type polyurethane resin is contained in a photochromic layer, both a color development speed and a color disappearance speed are low, and thus that photochromic laminate is insufficient.

Moreover, also in photochromic lenses, various processes such as direct kneading into a resin and coating on a resin surface have been tried. However, they

2

coated film and the control of thickness of a coated film in a photochromic layer are excellent, by interposing a photochromic layer formed by curing a mixture of a two-liquid type polyurethane of a polyurethane prepolymer and a curing agent, <u>and</u> a photochromic organic compound.[[,]] <u>Optionally,</u> a light stabilizer and an antioxidant between two transparent synthetic resin layers <u>may be used.</u>~~, to accomplish the present invention.~~

That is, the present invention provides a transparent synthetic resin laminate with photochromism property consisting essentially of two transparent synthetic resin layers and a photochromic layer formed by curing a mixture of a two liquid polyurethane of a polyurethane prepolymer and a curing agent, ~~and~~ a photochromic organic compound, ~~and further~~ a light stabilizer and an antioxidant ~~which is interposed~~ between ~~said~~ two transparent synthetic resin layers.

Further, the present invention provides a process for producing a transparent synthetic resin laminate with photochromism property which comprises:

coating a mixture of a two-liquid polyurethane of a polyurethane prepolymer and a curing agent, a photochromic organic compound and a solvent, ~~and further~~ a light stabilizer, and an antioxidant on one side of a transparent synthetic resin sheet,

then, removing <u>substantially all</u> the solvent from the mixture ~~to a state not to contain substantially the solvent,~~

4

then, adhering another transparent synthetic resin sheet to the coated side of said synthetic resin sheet, and

then, curing the two-liquid polyurethane,

thereby, forming a photochromic layer.

The present invention will be described in detail below.

The transparent synthetic resin to be used in the present invention is not limited as long as it is a resin with high transparency. It is preferable to use a polycarbonate resin and a polymethylmethacrylate resin. As the combination of two transparent synthetic resins, a polycarbonate resin, a polymethylmethacrylate or both thereof is (are) applied to the two transparent synthetic resins. A transparent synthetic resin with a thickness of 50 to 2000 μm is applied may be used. Particularly, wWhen bending into a lens form is performed, it is preferable to use a synthetic resin sheet with a thickness of 100 to 1000 μm.

In tThe present invention, there is provided relates to a photochromic layer formed by cure of a two-liquid polyurethane of a polyurethane prepolymer and a curing agent containing a photochromic organic compound, a light stabilizer, and an antioxidant which is interposed between two transparent synthetic resin layers. Thereby, it becomes possible to produce industrially a transparent synthetic resin laminate excellent in both heat resinstance and impact resistance which that exhibits a high color development speed and a high color disappearance speed in use

as a lens and possesses photochromic performance <u>that is</u> excellent in surface smoothness of a coated film in a photochromic layer, equivalent to conventional inorganic types, and maintains ~~a~~ photochromic characteristics, such as contrast in color development, for a long <u>period of</u> time.

Generally, polyurethane includes one-liquid type and two-liquid type. In the present invention, it is preferable ~~to use a two-liquid polyurethane of a polyurethane prepolymer and a curing agent~~ from the aspects of color development speed, ~~and~~ color disappearance speed, and solubility of photochromic compound and various additives <u>to use a two liquid polyurethane of a polyurethane prepolymer and a curing agent</u>. Actually, a prepolymer is dissolved in a specific solvent and mixed with various additives including a photochromic compound and then a curing agent is added thereto.

As the polyurethane prepolymer, a compound obtained by reaction of isocyanate and polyol in a specific proportion is used. That is, the polyurethane prepolymer is a compound with an isocyanate group on both ends obtained from diisocyanate and polyol. ~~As t~~<u>T</u>he diisocyanate compound to be used for the polyurethane prepolymer[[,]] <u>is preferably</u> diphenylmethane-4,4'-diisocyanate (MDI)<u>.</u>~~is preferable.~~ Further, as the polyol, it is preferable to use polypropylene glycol (PPG) with a polymerization degree of 5 to 30.

The molecular weight of the polyurethane prepolymer is a number average molecular weight of 500 to 5000 and preferably 1500 to 4000 and more preferably 2000 to 3000.

~~On the other hand, t~~The curing agent is not limited as long as it is a compound with two hydroxyl groups. Examples of the curing agent include polyurethane polyol, polyether polyol, polyester polyol, acryl polyol, polybutadiene polyol and polycarbonate polyol, among which polyurethane polyol with a hydroxyl group on its end, obtained from specific isocyanate and specific polyol, is preferable. Particularly, polyurethane polyol with a hydroxy group on at least both ends derived from diisocyante and polyol is preferable and it is preferable to use tolylenediisocyanate (TDI) as the diisocyanate. Further, as the polyol, it is preferable to use PPG with polymerization degree of 5 to 30.

The molecular weight of the curing agent is a number average molecular weight of 500 to 5000 and preferably 1500 to 4000 and more preferably 2000 to 3000.

In order to adjust the viscosity of the polyurethane prepolymer and the curing agent, a solvent such as ethyl acetate and tetrahydrofurane may be used.

In the present invention, the organic compound with photochromic property is not limited as long as it has good compatibility with the polyurethane prepolymer. Photochromic organic compound obtainable on the market can be used. From the aspect of photochromic performance ~~As the photochromic organic~~

7

~~compound,~~ spiropyran compounds, spiroxazine compounds, and naphthopyran

compounds are preferably used as the <u>photochromic organic compound</u> ~~from the~~

~~aspect of photochromic performance.~~

Examples of the spiropyran compound include 1',3',3'-trimethylspiro(2H-1-

benzopyran-2,2'-indoline), 1',3',3'-trimethylspiro-8-nitro(2H-1-benzopyran-2,2'-

indoline), 1',3',3'-trimethyl-6-hydroxyspiro(2H-1-benzopyran-2,2'-indoline), 1',3',3'-

trimethylspiro-8-methoxy(2H-1-benzopyran-2,2'-indoline), 5'-chloro-1',3',3'-trimethyl-

6-nitrospiro(2H-1-benzopyran-2,2'-indoline), 6,8-dibromo-1',3',3'-trimethylspiro(2H-

1-benzopyran-2,2'-indoline), 8-ethoxy-1',3',3',4',7'-pentamethylspiro(2H-1-

benzopyran-2,2'-indoline), 5'-chloro-1',3',3'-trimethylspiro-6,8-dinitro(2H-1-

benzopyran-2,2'-indoline), 3,3,1-diphenyl-3H-naphtho(2,1-b) pyran, 1,3,3-

triphenylspiro[indoline-2,3'-(3H)-naphtho(2,1-b)pyran], 1-(2,3,4,5,6-

pentamethylbenzyl)-3,3-dimethylspiro[indoline-2,3'-(3H)-naphtho(2,1-b)pyran], 1-(2-

methoxy-5-nitrobenzyl)-3,3-dimethylspiro[indoline-2,3'-naphtho(2,1-b)pyran], 1-(2-

nitrobenzyl)-3,3-dimethylspiro[indoline-2,3'-naphtho(2,1-b)pyran], 1-(2-

naphthylmethyl)-3,3-dimethylspiro[indoline-2,3'-naphtho(2,1-b)pyran] and 1,3,3-

trimethyl-6'-nitro-spiro[2H-1-benzopyran-2,2'-[2H]-indole].

Examples of the spiroxazine compound include 1,3,3-trimethylspiro [indolino-

2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 5-methoxy-1,3,3-trimethylspiro [indolino-

2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 5-chloro-1,3,3-trimethylspiro [indolino-2,3'-

[3H] naphtho [2,1-b] [1,4] oxazine], 4,7-diethoxy-1,3,3-trimethylspiro [indolino-2,3'-

[3H] naphtho [2,1-b] [1,4] oxazine], 5-chloro-1-butyl-3,3-dimethylspiro [indolino-2,3'-

[3H] naphtho [2,1-b] [1,4] oxazine], 1,3,3,5-tetramethyl-9'-ethoxyspiro [indolino-2,3'-

[3H] naphtho [2,1-b] [1,4] oxazine], 1-benzyl-3,3-dimethylspiro [indoline-2,3'-[3H]

naphtho [2,1-b] [1,4] oxazine], 1-(4-methoxybenzyl)-3,3-dimethylspiro [indoline-2,3'-

[3H] naphtho [2,1-b] [1,4] oxazine], 1-(2-methylbenzyl)-3,3-dimethylspiro [indoline-

2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 1-(3,5-dimethylbenzyl)-3,3-dimethylspiro

[indoline-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 1- (4-chlorobenzyl)-3,3-

dimethylspiro [indoline-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 1-(4-bromobenzyl)-

3,3-dimethylspiro [indoline-2,3'-[3H] naphtho [2,1-b] [1,4] oxazine], 1-(2-

fluorobenzyl)-3,3-dimethylspiro [indoline-2,3'-[3H] naphtho[2,1-b] [1,4] oxazine],

1,3,5,6-tetramethyl-3-ethylspiro [indoline-2,3'-[3H] pyrido [3,2-f] [1,4]-benzoxazine],

1,3,3,5,6-pentamethylspiro [indoline-2,3'-[3H] pyrido [3,2-f] [1,4]-benzoxazine], 6'-

(2,3-dihydro-1H-indole-1-yl)-1,3-dihydro-3,3-dimethyl-1-propyl-spiro [2H-indole-2,3'-

[3H] naphtho [2,1-b] [1,4] oxazine], 6'-(2,3-dihydro-1H-indole-1-yl)-1,3-dihydro-3,3-

dimethyl-1-(2-methylpropyl)-spiro [2H-indole-2,3'-[3H]-naphtho [2,1-b]

[1,4]oxazine], 1,3,3-trimethyl-1-6'-(2,3-dihydro-1H-indole-1-yl)-spiro [2H-indole-2,3'-

[3H]-naphtho [2,1-b] [1,4] oxazine], 1,3,3-trimethyl-6'-(1-piperidinyl)-spiro [2H-

indole-2,3'-[3H]-naphtho [2, 1-b] [1,4] oxazine], 1,3,3-trimethyl-6'-(1-piperidinyl)-

spiro [2H-indole-2,3'-[3H]-naphtho[2,1-b] [1,4] oxazine], 1,3,3-trimethyl-6'-(1-

piperidinyl)-6-(trifluoromethyl)-spiro [2H-indole-2,3'-[3H]-naphtho [2,1-b] [1,4]

oxazine] and 1,3,3,5,6-pentamethyl-spiro [2H-indole-2,3'-[3H]-naphtho [2,1-b] [1,4]

oxazine].

9

Examples of the naphthopyran compound include 3,3-diphenyl-3H-naphtho [2,1-b] pyran, 2,2-diphenyl-2H-naphtho [1,2-b] pyran, 3-(2-fluorophenyl)-3-(4-methoxyphenyl)-3H-naphtho [2, 1-b] pyran, 3-(2-methyl-4-methoxyphenyl)-3-(4-ethoxyphenyl)-3H-naphtho [2, 1-b] pyran, 3-(2-furil)-3-(2-fluorophenyl)-3H-naphtho [2,1-b] pyran, 3-(2-thienyl) -3-(2-fluoro-4-methoxyphenyl)-3H-naphtho [2,1-b] pyran, 3-{2-(1-methylpyrrolidinyl)}-3-(2-methyl-4-methoxyphenyl)-3H-naphtho [2,1-b] pyran, spiro (bicyclo [3.3.1] nonane-9,3'-3H-naphtho [2,1-b] pyran), spiro (bicyclo [3.3.1] nonane-9-2'-3H-naphtho [2,1-b] pyran), 4-[4-[6-(4-morpholinyl)-3-phenyl-3H-naphtho [2,1-b] pyran-3-yl] phenyl]-morpholine, 4-[3-(4-methoxyphenyl)-3-phenyl-3H-naphtho [2, 1-b] pyran-6-yl]-morpholine, 4-[3,3-bis(4-methoxyphenyl)-3H-naphtho [2,1-b] pyran-6-yl]-morpholine, 4-[3-phenyl-3-[4-(1-piperidinyl) phenyl]-3H-naphtho [2, 1-b] pyran-6-yl]-morpholine and 2,2-diphenyl-2H-naphtho [2,1-b] pyran.

In order to ensure the life of the synthetic resin laminate of the present invention, it is necessary to add various stabilizers. As the stabilizer, light stabilizers, such as hindered amines and antioxidants such as hindered phenols are added.

Examples of the hindered amine include bis(2,2,6,6-tetramethyl-4-piperidinyl) sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidinyl)-[[3,5-bis(1,1-dimethylethyl)]-[4-hydroxyphenyl]methyl]butyl malonate, 1-(methyl)-8-(1,2,2,6,6-pentamethyl-4-piperidinyl)-sebacate, 1-[2-(3-(3,5-di-t-butyl-4-hydroxyphenyl) propionyloxy)ethyl]-4-

10

[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy]-2,2,6,6-tetramethylpiperidine, 4-benzoyloxy-2,2,6,6-tetramethylpiperidine, triethylene-diamine and 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4,5]decane-2,4-dione. As other nickel ultraviolet ray stabilizer, [2,2'-thiobis(4-t-octylphenolate)]-n-butylamine nickel, nickel complex-3,5-di-t-butyl-4-hydroxybenzyl·phsosphoric acid monoethylate and nickel·dibutyl carbamate also can be used. A tertiary hindered amine compound is preferable. Particularly, as a hindered amine light stabilizer of[[,]] bis(1,2,2,6,6-pentamethyl-4-piperidinyl)-sebacate or a condensation product of 1,2,2,6,6-pentamethyl-4-piperidinol, tridodecyl alcohol, and 1,2,3,4-butanetetra caboxylic acid, as tertiary hindered amine compound is preferable.

Examples of the antioxidant include 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl) butane, 2,2'-methylenebis (4-ethyl-6-t-butylphenol), tetrakis-[methylene-3-(3',5'-di-t-butyl-4'-hydroxyphenyl) propionate]methane, 2,6-di-t-butyl-p-cresol, 4,4'-butylidenebis(3-methyl-6-t-butylphenol), 1,3,5-tris(3', 5'-di-t-butyl-4'-hydroxybenzyl)-S-triazine-2,4,6-(1H, 3H, 5H)trione, stearyl-ß-(3,5-di-t-butyl-4-hydorxyphenyl)propionate, 1,3,5-tris(4-t-butyl-3-hydroxy-2,6-dimethylbenzyl) isocyanuric acid, 4,4'-thiobis(3-methyl-6-t-butylphenol) and 1,3,5-trimethyl-2,4,6-tris (3,5-di-t-butyl-4-hydroxybenzyl) benzene.

Particularly, as a phenol antioxidant[[,]] of 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl) butane tetrakis-[methylene-3-(3',5'-di-t-butyl-4'-hydroxyphenyl) propionate] methane and 1,3,5-tris(3,5-di-t-butyl-4-hyroxybenzyl)-1,3,5-triazine-

2,4,6-(1H, 3H, 5H)-trione, which contains 3 or more ~~above of~~ hindered phenols, is ~~are~~ preferable.

The transparent synthetic resin laminate with photochromic property of the present invention is produced according to the ~~below~~ process below. A photochromic organic compound is added in the proportion of 0.2 to 5 % to resin solid matter ~~to~~ in a solution of a polyurethane prepolymer diluted with specific organic solvent and an additive(s) of hindered amine light stabilizer and/or antioxidant is (are) ~~further~~ added thereto in the proportion of 0.1 to 5 % to resin solid matter and uniformly mixed with stirring. Then, a curing agent is ~~further~~ added thereto in a I/H ratio of isocyanate group (I) to hydroxyl group (H) ~~of the curing agent~~ of 0.9 to 20, and preferably 1 to 10, ~~as a standard~~ and stirring is further performed to form a solution. It is suitable that the polymer concentration in the solution thus obtained is ~~usually~~ 40 to 90 % by weight. The solution is coated with a doctor blade of coating thickness 100 to 1000 μm on one side of a transparent synthetic resin sheet. After the completion of coating, heat drying is performed to the state substantially not containing the solvent on the coated surface and another transparent synthetic resin sheet is adhered to the coated surface of said synthetic resin sheet in a sandwich form. The above-mentioned heat drying is usually performed at 20 to 50°C for 5 to 60 minutes. A laminate sheet thus obtained is heated to cure the polyurethane prepolymer containing the curing agent, whereby a transparent

12

synthetic resin laminate is obtained. The curing conditions of the polyurethane prepolymer are usually 60 to 140 °C and 2 hours to 1 week.

Examples of the solvent include hydrocarbons such as hexane, heptane, octane, cyclohexane, toluene, xylene and ethyl benzene, esters such as ethyl acetate, methyl acetate, isopropyl acetate, n-propyl acetate, isobutyl acetate, n-butyl acetate, isoamyl acetate, methyl propionate and isobutyl propionate, ketones such as acetone, methylethyl ketone, diethyl ketone, methylisobutyl ketone, acetyl acetone and cyclohexyl ketone, ether esters such as cellosolve aetate, diethylglycol diaetate, ethyleneglycol mono n-butylether acetate, propylene glycol and monomethylether acetate, tertiary alcohols such as diacetone alcohol and t-amyl alcohol and tetrahydofuran. Particularly, ethyl aetate, tetrahydrofuran and toluene are preferable.

BEST MODE FOR CARRYING OUT THE INVENTION

The present invention will be described in more detail below, referring to Examples, which are not intended to limit the scope of the present invention.

Examples 1 to 4

2 % of Photochromic compound 1 or 2 per to resin solid matter and 1 to 2 % of Additive 1 per to resin solid matter were dissolved in a solution of 15 g of a

polyurethane precursor having a NCO group equivalent weight (equivalent weight is the [[:]] average molecular weight per one functional group) of 1500 obtained by reaction of diphenylmethane-4,4'-diisocyanate and polypropylene glycol having an average polymerization degree of 15 diluted with 8.3 g of tetrahydrofuran and stirred until uniformity was ensured and then 3 g of a curing agent having a hydroxyl group equivalent weight of 1050 obtained by reaction of tolylene diisocyanate and polypropylene glycol having an average polymerization degree of 10 was added thereto and further stirred.

The solution thus obtained was coated with a doctor blade of coating thickness 400 μm, manufactured by Yoshimitsu Seiki K.K., in Japan on a polycarbonate film of thickness 700 μm (trade name IUPILON, manufactured by Mitsubishi Gas Chemical Co., Inc.). After the completion of coating, the solvent was vaporized at 45 °C for 10 minutes in a hot air dryer and the polycarbonate film was adhered to make a sheet form and then heat curing was performed at 70 °C for 2 days. The mMeasurements of the transmittance in maximum absorption wave length and the evaluation of the light resistance for the synthetic resin laminate thus obtained were performed and the thickness of the photochromic layer was measured and its appearance was observed. The proportion of each component for the formation of the laminates was shown in Table 1. The evaluation results of the laminated laminates were shown in Table 2.

Photochromic compound 1:

1,3-dihydro-1,3,3,5,6 (1,3,3,4,5) pentamethyl-spiro[2H-indole-2,3-[3H]-naphtho[2,b] [1,4]oxazine]

Photochromic compound 2:

3,3-diphenyl-3H-naphtho [2, 1-b] pyran

Additive 1:

bis (2,2,6,6-tetramethyl-4-piperidinyl) sebacate

Each performance was evaluated according to the following methods.

[Measurement of transmittance]

A single wave length light of 360 nm was irradiated with an ultramonochromatic light source. ~~and t~~Transmittance after 5 minutes from the start~~ing~~ of the irradiation and transmittance with ~~in~~ non-irradiation were measured. A spectrophotometer, manufactured by Nihon Bunko k.k., ~~in~~ Japan, was used in the measurement of transmittance and transmittance in maximum absorption wave length was measured.

[Evaluation of light resistance]

Contrast prior to exposure and contrast after exposure ~~for 60 hours~~ to a sunshine weather meter for 60 hours under ~~below~~ the conditions below were

15

measured. In order to compare with contrast prior to exposure, contrast retention percentage was calculated to evaluate its life.

(1) Setting conditions of sunshine weather meter

    · Irradiance: 255 w/m^2 (300 to 700 nm)
    · Temperature: room temperature
    · Rainfall was not applied.

(2) Calculation of contrast retention percentage (%)

Contrast retention percentage (%)
$$= (L^*_3 - L^*_4) \times 100/(L^*_1 - L^*_2)$$

    · L^*_1 : contrast prior to light resistance test
      (in ultraviolet light non-irradiation)
    · L^*_2 : contrast prior to light resistance test
      (in ultraviolet light irradiation)
    · L^*_3 : contrast after light resistance test
      (in ultraviolet light non-irradiation)
    · L^*_4 : contrast after light resistance test
      (in ultraviolet light irradiation)

(3) Evaluation
    Contrast life was evaluated based on the following criterion.

    ○ : contrast retention percentage after light
      resistance test is 70 % or above.

16

Δ : contrast retention percentage after light

resistance test is below 70 %.

[Color development speed and color disappearance speed]

Color development speed (ta) and color disappearance speed (tb) were

measured as below.

T1 : transmittance in non-irradiation of

ultraviolet light

T2 : transmittance in irradiation of ultraviolet

light

ta : a time in which transmittance is changed from

T1 to (T1+T2)/2 by irradiation of ultraviolet

light

tb : a time in which transmittance is changed from

T2 to (T1+T2)/2 by shielding irradiated

ultraviolet light

Both ta and tb were determined by a curve of change of transmittance in

maximum absorption wave length with the lapse of time.

Comparative Example 1

The synthetic resin laminate was obtained in the same experiment as in

Example 1, except that the urethane was changed to solvent type one-liquid,

Hamatai Y-7122-A, manufactured by Yokohama Gomu k.k., in Japan. The proportion of each component was shown in Table 1 and the evaluation results were shown in Table 2.

Examples 5 to 12

1 % of Photochromic compound 3 per to resin solid matter[[,]] and 0.5 % of Photochromic compound 4 per to resin solid matter were added to a solution of 15 g of a polyurethane precursor diluted with 13.6 g of an organic solvent (toluene 4.6 g, methylethyl ketone 1.8 g and ethyl acetate 7.2 g) in the same manner as in Example 1 and each of the Additives 1 to 4 was further added thereto in the blend proportion shown in Table 3 and dissolved and 1.6 g of the same curing agent as in Example 1 was added thereto and stirred.

The solution thus obtained was coated with a doctor blade of coating thickness 300 μm, manufactured by Yoshimitsu Seiki k.k., in Japan, on a polycarbonate film of thickness 300 μm (trade name IUPILON, manufactured by Mitsubishi Gas Chemical Co., Inc.). After the completion of coating, the solvent was vaporized at 45 °C for 10 minutes in a hot air dryer. Another polycarbonate film of 300 μm was adhered thereto to make a sheet form and heat curing was performed at 70 °C for 3 days. The same evaluation as in Example 1 was performed for the synthetic resin laminate thus obtained. In the evaluation of light resistance, the evaluation was performed by changing the apparatus and further increasing

18

ultraviolet light radiant intensity. The evaluation results were shown in Table 4.

Further, when the samples thus prepared were exposed to sun light, they ~~presented~~

turned brown, and when they were put in a dark place, color disappearance

occurred.

Organic Photochromic compound 3 :

    4-[4-[6-(4-morpholynyl)-3-phenyl-3H-naphtho [2,1-b] pyran-3-yl] phenyl]-morpholine

Organic Photochromic compound 4 :

    1,3-dihydro-1,3,3,5,6(1,3,3,4,5)-pentamethyl-spiro(2H-indole-2,3-[3H]-naphtho[2,b] [1,4]oxazine]

Additive 1 : the same as in Example 1

    bis (2,2,6, 6—tetramethyl-4-piperidinyl) sebacate

Additive 2 :

    bis (1,2,2,6, 6-pentamethyl-4-piperidinyl) sebacate

Additive 3 :

    bis(1,2,2,6,6-pentamethyl-4-piperidinyl) sebacate

    1-(methyl)-8-(1,2,2,6,6-pentamethyl-4-piperidinyl)-sebacate

19

Additive 4 :

1,1,3-tris (2-methyl-4-hydroxy-5-t-butylphenyl) butane

The {measurement of transmittance} and the measurement and evaluation of {color development speed and color disappearance speed} was were performed in the same manner as in Example 1.

[Evaluation of light resistance]

As the evaluation, a A UV lamp was irradiated for 5 minutes prior to light resistance test and after light resistance test and then contrast due to color development and color difference were measured and contrast retention percentage and color change degree in color disappearance in the light resistance test were calculated. Thus, light resistance was evaluated. In the light resistance test, an apparatus with a xenon lamp as the light source (apparatus name SUNTEST CPS+, maker : manufactured by ATLAS) was used and an irradiance of 750 W/m^2 (300 to 800 nm) for 20 hours was applied. Further, the UV lamp had a single wave length of 360 nm in an ultramonochromatic light source (Nihon Bunko k.k., in Japan)

① Calculation of contrast retention percentage

It was calculated in the same method as in Example 1.

② Calculation of color change degree

20

color change degree

$$=[(L^*_1-L^*_3)^2+(a^*_1-a^*_3)^2+(b^*_1-b^*_3)^2]^{1/2}$$

· a^*_1 : a* value prior to light resistance test
  (ultraviolet light non-irradiation)
· a^*_3 : a* value after light resistance test
  (ultraviolet light non-irradiation)
· b^*_1 : b* value prior to light resistance test
  (ultraviolet light non-irradiation)
· b^*_3 : b* value after light resistance test
  (ultraviolet light non-irradiation)

③ Evaluation

O: After light resistance test, contrast is 70 %
  or above and color change degree is below 5 %.

△ : After light resistance test, contrast is below
  70 % and color change degree is 5 % or above.

INDUSTRIAL APPLICABILITY

In the formation of a polyurethane layer on a transparent synthetic resin surface, a polyurethane layer could be formed without impairing any photochromic performance by using specific two-liquid thermosetting poyurethane and mixing a polyurethane prepolymer, a curing agent and various additives including a photochromic compound in specific solvent and a transparent synthetic resin laminate with photochromism property to provide high availability could be produced efficiently by ensuring substantially non-solvent state thereof, and then adhering another transparent synthetic resin, and then performing heat cure. Further, a plastic lens with high photochromic performance and smooth photochromic layer could be obtained readily by using the laminate.

Table 1

	Polyurethane precursor (g)	Curing agent (g)	THF (Note 1) (g)	Species of photochromic compound	Concentration of photochromic compound (g)	Additive	Concentration of additive (%)
Example 1	15	3	8.3	1	2	1	1
2	15	3	8.3	1	2	1	2
3	15	3	8.3	2	2	1	1
4	15	3	8.3	2	2	1	2
Comp.Ex.1	30 (Note 2)	—	—	1	2	1	1

Note 1 : tetrahyrofuran

Note 2 : solvent type one-liquid

23

Table 2

	Thickness of Photo-chromic layer (μm)	Color in color develop-ment	Maximum absorption wave length (nm)	Maximum Transmittance in maximum absorption wave length ultraviolet light — in non-irradiation (%)	Maximum Transmittance in maximum absorption wave length ultraviolet light — in irradiation (%)	Color develop-ment speed ta (sec)	Color disapp-earance speed tb (sec)	Appea-rance	Life
Example 1	177	blue	620	83	58	13	13	good	○
2	178	blue	620	83	58	13	13	good	○
3	181	yellow	440	87	65	10	10	good	○
4	179	yellow	440	88	65	10	10	good	○
Comp.Ex.1	175	blue	620	80	52	23	26	good	△

24

Table 3

	Polyurethane precursor (g)	Curing agent (g)	Toluene MEK (Note 3) ethyl acetae	Photochromic compound species	concentration (%)	Additive light stabilizer species	concentration (%)	antioxidant species	concentration (%)
Example 5	15	1.6	13.6	3	1.0	2	3.0	—	—
				4	0.5				
Example 6	15	1.6	13.6	3	1.0	2	3.0	4	3.0
				4	0.5				
Example 7	15	1.6	13.6	3	1.0	3	3.0	—	—
				4	0.5				
Example 8	15	1.6	13.6	3	1.0	3	3.0	4	3.0
				4	0.5				
Example 9	15	1.6	13.6	3	1.0	1	3.0	—	—
				4	0.5				
Example 10	15	1.6	13.6	3	1.0	3	15.0	—	—
				4	0.5				
Example 11	15	1.6	13.6	3	1.0	3	15.0	4	3.0
				4	0.5				
Example 12	15	1.6	13.6	3	1.0	—	—	—	—
				4	0.5				

Note 3 : methylethyl ketone

Table 4

	Thickness of photochromic layer (µm)	Maximum absorption wave length (nm)	Transmittance in maximum absorption wave length in ultraviolet light		Color development speed ta (sec)	Color disappearance speed tb (sec)	Appearance	contrast retention percent (%)	Life	
			in non-irradiation (%)	in irradiation (%)					color change degree	Evaluation
Example 5	133	460	84	63	13	15	good	72	3	O
Example 6	140	460	84	65	14	16	good	74	2	O
Example 7	137	460	85	61	14	16	good	70	4	O
Example 8	128	460	84	67	14	16	good	73	3	C
Example 9	136	460	85	65	13	15	good	43	7	△
Example 10	132	460	85	63	14	16	good	51	4	△
Example 11	135	460	84	66	14	16	good	56	3	△
Example 12	138	460	85	67	13	15	good	34	10	△

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : Chiharu NISHIZAWA, et al.

Serial No. : 09/980,010

Filed : November 30, 2001

For : TRANSPARENT SYNTHETIC RESIN LAMINATE

WITH PHOTOCHROMISM PROPERTY

Art Unit : 1711

D E C L A R A T I O N

Honorable Commissioner of

Patent & Trademarks

Washington, D.C. 20231

I, Kenji KOUNO, Japanese citizen, residing at c/o Mitsubishi Gas Chemical Company Inc., Corporate Research Laboratory, 22 Wadai, Tsukuba-shi, Ibaraki-ken 300-4247 Japan, Declare:

That I am an inventor of the above application, and familiar with the invention and prosecution history of said application ;

I performed comparative experiments in order to demonstrate that it is far more difficult to form a lens by bending the transparent synthetic resin laminate used the curing agent (tri-methylol propane) disclosed in Ormsby et al

1

(USP No. 4,889,413) than in the case used the transparent synthetic resin laminate of the present invention.

Experiment
Example 1.

Ten discs of 75 mm φ were prepared from the transparent synthetic resin laminate obtained in Example 1 by drawing. The ten discs thus obtained were dried at 65℃ for 24 hours in a hot wind drier.

These discs were heat bended using a mold with a curve surface (R=65.38mm) and press molded at a mold temperature of 138℃ for 3 seconds.

Thus, ten lenses were normally formed without causing leakage of the photochromic layer from each discs.

Comparative Example 6

The same experiment as in Example 1 of the present invention was performed except that 3g of tri-methylol propane was used instead of 3g of the curing agent of Example 1.

Then, ten discs thus obtained were heat bended and press molded in the same manner as in Example 1.

In seven discs among the ten discs, leakage of the photochromic layer from each discs occurred due to peeling-off of the photochromic layer from the polycarbonate films as outer layers, so that lenses could not be formed.

2

Conclusion

It was far more difficult to form a lens by bending the transparent synthetic resin laminate used the curing agent (tri-methylol propane) disclosed in Ormsby et al than in the case of used the transparent synthetic resin laminate of the present invention.

The undersigned declarant declares further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this day of December 1 , 2003

Kenji Kouno

Kenji KOUNO

4

Chemical Survey (quarterly publication), No. 28, " Chemistry of Organic Photochromism", edited by the Chemical Society of Japan, published on May 30, 1996 by the Society Publication Center.

(Page 51, lines 13 to 17)
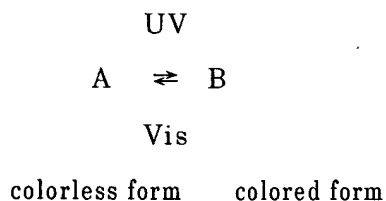
$$A \underset{\text{Vis}}{\overset{\text{UV}}{\rightleftharpoons}} B$$

colorless form   colored form

As described in the above formula, photochsomism is defined as "the phenomena that a single chemical species reversibly isomerizes between two states different in absorption spectrum to each other without changing its molecular weight by action of a light.

Organic photochromic compounds focusing attention as an optical information memory element used a laser beam repeat color development‑color disappearance by changing a wave length of a light for irradiation.

(Page 53, paragraph 1. 2, lines 7 to 9)

The life of the colored species is short in a dark place at a room temperature and its half value period ($\tau_{1/2}$,min) is 1/2 or below irrelevantly to species of N‑site substituted group.

A portion of data thereof was shown in Figure 3.

(Page 55, Figure 3)

1

spiropyrane   merocyanine A   merocyanine B

R	In MeOH		In acetone	
	$\lambda_{max}/$ nm	$\tau_{1/2}/$ min	$\lambda_{max}/$ nm	$\tau_{1/2}/$ min
Me	588	0.2	673	0.1
CHMe₂	581	0.8	652	0.5
C₁₈H₃₇	590	0.6	660	0.6

有機フォトクロミズムの化学

日本化学会編

目　　　次

I　フォトクロミズムの物理化学

II　フォトクロミック化合物の化学

III　フォトクロミズムの応用展開

4 スピロピラン類

宮　下　　晃

　現情報化社会において多種類の情報を取り扱うソフトおよび高速処理を可能にするハードウェア両面における技術革新は目覚ましく，複雑な情報の高速転送と高密度記録化技術の確立が研究開発の主要ストラテジーとなっている．とくに，デバイス科学分野においてもエレクトロニクスから光エレクトロニクスの時代に移行し，そして最近では次世代超高速高密度記憶分子素子工学を担うフォトニクス（光子工学）関連研究が大変重要であり非常に注目されている．最近，これらの基礎物理学的な要請に応える属性を有するものとして光応答性有機化合物が大変注目されており，それらの属性はまさに光子を伝達因子またはトリガーとした次世代分子素子に適している．

　とくに，光応答性有機色素の中でもフォトクロミズムを示す有機化合物の開発が最も活発であり，現在求められているデバイス機能に合致した有機化合物の分子設計および合成研究が産学とも非常に活発である．

$$A \underset{\text{Vis}}{\overset{\text{UV}}{\rightleftarrows}} B$$

colorless form　　colored form
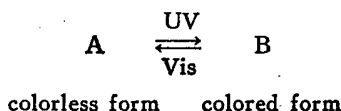
　フォトクロミズムとは，上式に示したように「単一の化学種が光の作用により分子量を変えることなく吸収スペクトルの異なる2つの状態間を可逆的に異性化する現象」と定義される[1]．最近，レーザー光を用いた光情報記憶素子として注目されている有機フォトクロミック化合物は，照射光波長を変化させることで発色-消色を繰り返すが，多くの場合，発色型構造Bが熱的にきわめて不安定であることやそれらの吸収帯域が半導体レーザー波長域にまで達していないこと，さらに発色-消色の繰り返し耐久性が低いなど多くの解決すべき問題が残っており実用化開発が遅れている．

　現在，数多くのフォトクロミック化合物が合成され，それらの光特性が研究されているが，それらの約半数はスピロピラン系フォトクロミック材料に関するものである．スピロピラン（またはスピロクロメン）は，基本的にはそれらの分子構造中に2つのヘテロ環状部をもち，それらがお互いに共通の正4面体型 sp^3-炭素原子で結合している．したがって，これら2つのヘテロ環状部を含む面はお互いに直行している．これら一般的な定義に分類されるスピロピラン類は，現在までのところ50種類にも及ぶ構造で8500種の化合物が合成され，基礎研究および応用開発両面から最も活発に研究されている機能性色素の1つであるといえる．スピロピラン類がサーモクロミズムを示すことは，すでに1921年に発見されていたが，それらがフォトクロミズムを示すこ

とが報告されたのは30年後の1952年である．その後，これら光可逆的な変換反応が，コンピューターメモリーや密度可変型光シャッターの構築に応用できることが発表されて以来，世界中の企業や学術関連研究者の熱い注目を浴び活発に研究されてきた．とくに，スピロピラン類は，銀塩を用いない高解像写真や関連光学素子，可変型トランスミッション材料や photovoltaic やホログラフ材料，さらには，種々の光トリガーに対する非線形応答機能を付与したピコ秒単位で可逆的に応答する光分子素子の開発など，広い分野への応用が期待されている．最近では，スピロピラン類を用いた会合体や配向膜の特性を利用した 10 多重光記録が可能になり高密度光記録技術が確立しつつある[2]．

本章では，最近筆者らの研究グループで新規に分子設計した種々のスピロピラン誘導体についてそれらの合成ならびに結晶構造，正・逆フォトクロミック特性，準安定型溶液構造，そして側鎖型ポリマー化による準安定型の長期安定化についてそれらの概要を紹介する．

従来までのスピロピラン類の合成法，および光化学特性などについては，いくつかの総説や成書があるのでそれらを参照されたい[3]．

1 新規なスピロベンゾチオピランの合成とフォトクロミズム

1.1 合成と結晶構造

種々の置換基を有するスピロベンゾチオピラン**1**は，通常のスピロピラン合成法とその応用により収率よく得られる．1例として，筆者らの合成した 8′-methacryloxymethyl-3, 3-dimethyl-6′-nitrospiro[(2′H)-1′-benzothiopyran-2, 2′-indoline] の合成ルートを以下の反応スキームに示した[4]．
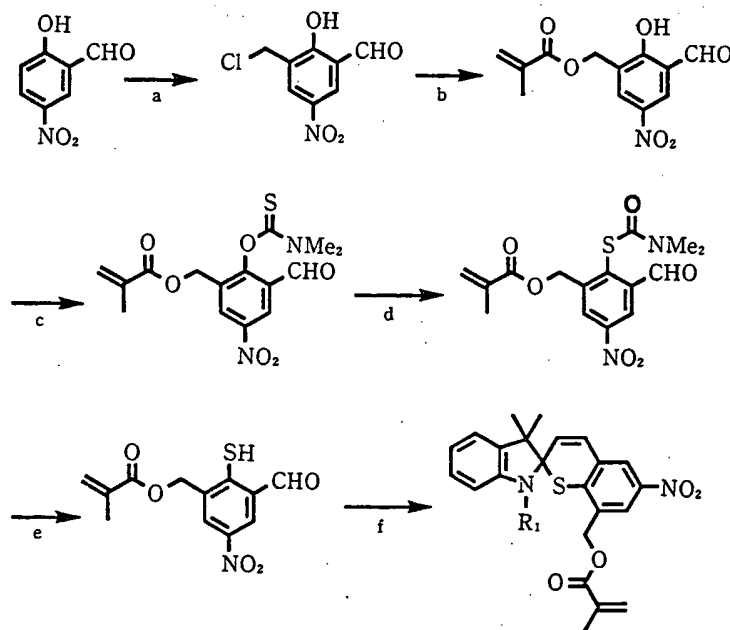
a) MeOCH₂Cl/AlCl₃, b) CH₂=C(Me)COOAg, c) Me₂NCSCl/1, 4-diazabicyclo [2.2.2]octane, d) refluxed in toluene, e) equimolar 0.7 M NaOH at 20°C then 1 M HCl, f) 1-alkyl-3, 3-dimethyl-2-methyleneindoline.
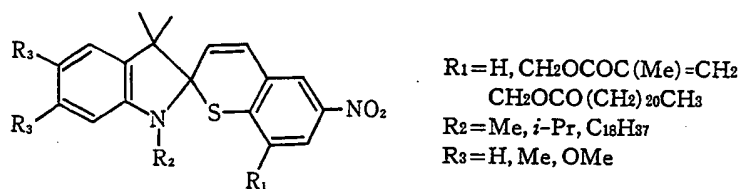
$R_1 = H, CH_2OCOC(Me)=CH_2$
$\qquad CH_2OCO(CH_2)_{20}CH_3$
$R_2 = Me, i\text{-}Pr, C_{18}H_{37}$
$R_3 = H, Me, OMe$

図 1

スピロ炭素周辺の構造環境を検討する目的で 8′ 位にメタクリロキシメチル基を有するスピロベンゾチオピランのX線結晶解析を行った. その結果, 図2の ORTEP 図に示すようにスピロ炭素とS原子間距離は 1.91Å と通常の C-S 単結合距離の 1.81Å より 0.1Å ほど長く, 後述するように紫外光トリガーによりスピロ炭素-S 結合が容易に切断する. 一方, 逆に硫黄原子とベンゾピラン環炭素 (9′ 位, C_{16}) との距離は 1.74Å と短く, より二重結合性を有していると考えられる.

この傾向はベンゾピラン環 6′ 位に NO_2 のような電子吸引性置換基が結合するとより顕著になり光照射による異性化反応が容易になる. また, インドリン環とベンゾピラン環は, スピロ炭素で直行しており, しかもこのスピロ炭素はこれら2つの環のなす平面構造からずれている[5].

図2の下にはスピロベンゾチオピランのスタッキング構造も示した. 中津らは, 種々のスピロピラン誘導体のX線結晶構造解析よりそれらの結晶状態における立体構造の特徴を詳しく検討し, とくに, スピロ炭素の周辺は原子が密集しておりファンデルワールス距離以下の非結合原子どうしの接触がみられることなど興味深い報告をしている[6].

1.2 フォトクロミズムと溶媒効果

スピロベンゾチオピラン1は無色から淡黄色結晶であり, 溶液中, 紫外光照射 (365 nm) により速やかに深緑色に着色する. また, この着色溶液は, 熱または, 可視光 (>500 nm) 照射により速やかに消色する正フォトクロミズムを示す. 1の紫外光照射により生成した着色種の吸収極大値は溶媒極性に大きく依存し, 極性の低いアセトン中ではメタノール中に比べ吸収極大が 71～85 nm 長波長シフトする.
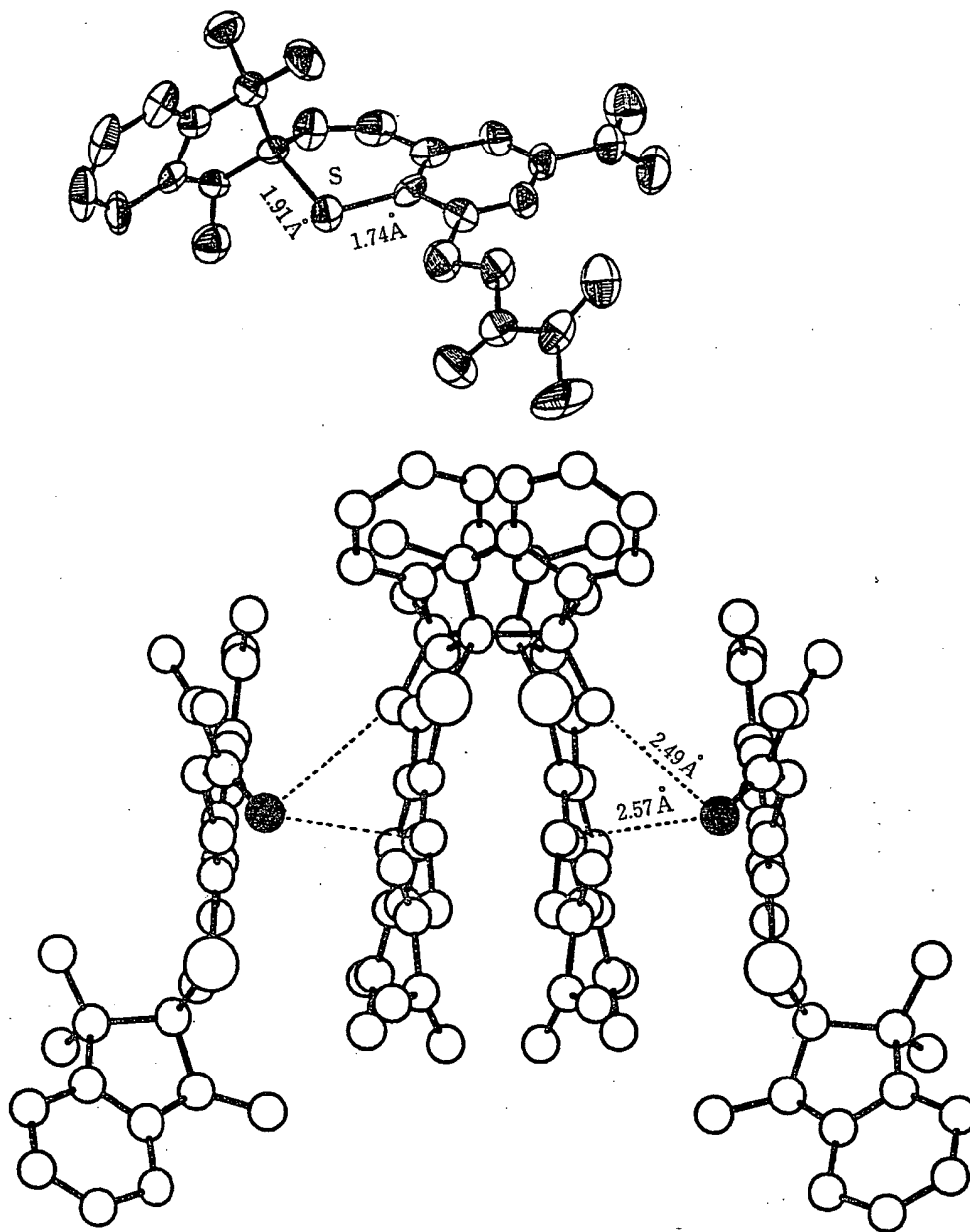
また, 着色種の暗所下室温における寿命は短くN位置換基の種類に無関係にその半減期 ($\tau_{1/2}$, min) は1分以下である.
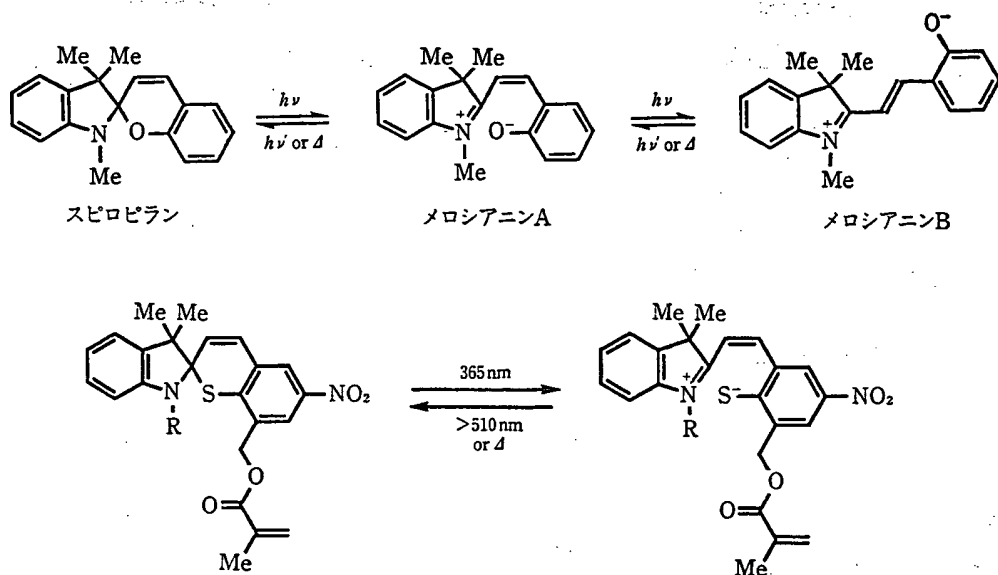
図3にその一部のデータを示した[4].

1.3 フォトメロシアニン着色種構造の理論的考察

無色系のスピロベンゾチオピランは, 紫外線照射によりスピロ炭素と硫黄原子間の結合をイオン開裂し, 鮮やかな緑色のメロシアニン (フォトメロシアニン) を生成する. このメロシアニンのスペクトルパターンは, 紫外線照射時の条件 (温度など) などで変化することが多く, これはメロシアニンA, B間のシス-トランス異性化反応により説明されている.

Crystal data of spirobenzothiopyran **1**

formula	$C_{24}H_{24}N_2O_4S$
formula weight	436. 52
crystal system	monoclinic
space group	*Pc*
$a/Å$	12. 893 (2)
$b/Å$	14. 117 (4)
$c/Å$	12. 222 (2)
β/deg	91. 91 (1)
$V/Å^3$	2223. 3 (8)
Z	4
$D_{calcd}/g\ cm^{-1}$	1. 305
$D_{found}/g\ cm^{-1}$	1. 31
R_w	0. 069

図 2

スピロピラン　　　　　　　　メロシアニンA　　　　　　　メロシアニンB

R	In MeOH		In acetone	
	$\lambda_{max}/$ nm	$\tau_{1/2}/$ min	$\lambda_{max}/$ nm	$\tau_{1/2}/$ min
Me	588	0.2	673	0.1
CHMe₂	581	0.8	652	0.5
C₁₈H₃₇	590	0.6	660	0.6

図 3

　また，フォトメロシアニンAにおける各原子の電荷を INDOMO 法により計算するとスピロ炭素に ＋0.24 e，ベンゾピラン環の酸素に −0.41 e が存在することから，消色反応はこれら原子間の静電引力によって誘起されるものと推定できる[6]．一方，玉置らは，種々の置換基を有するスピロピラン類のフォトメロシアニンへの光異性化反応機構を解明する目的で反応励起状態，量子収率および反応動力学的立場から詳しく検討し興味深い研究成果を報告している[7]．

　最近，筆者らは種々のヘテロ元素を分子骨格に含むスピロピラン誘導体を合成し，そのフォトクロミック特性を研究し報告してきた．とくに，スピロベンゾチオピランの発色種が

図 4　スピロベンゾチオピラン 1c のアセトン溶液中でのフォトクロミズム．実線は 1c に紫外光照射直後の電子スペクトル，破線は可視光照射後の電子スペクトル．

半導体レーザー域に吸収を有することに注目し，まず，その開環型発色体の可能な安定構造とそれらの最大吸収波長を ZINDO 法による分子軌道法計算により検討した．その結果，図5に示したように4つの異性体のうち (s-trans, s-cis) 型フォトメロシアニンが最も安定な構造になり，H₂O 中での最大吸収波長は 732 nm と計算された[8]．
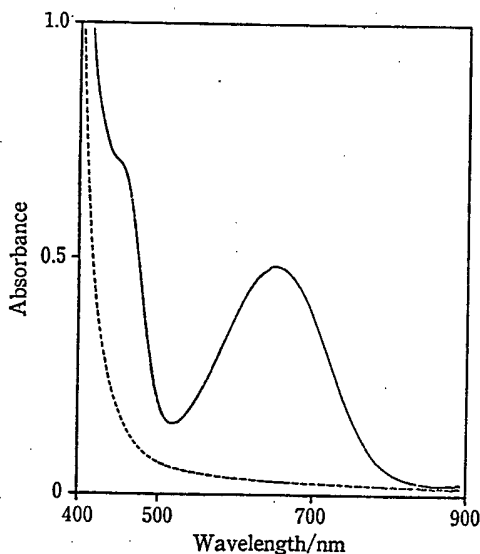
(s-*cis*,s-*cis*)

E-4.78 kcal mol⁻¹
λ_{max}=663nm

(s-*cis*,s-*trans*)

E-5.29 kcal mol⁻¹
λ_{max}=648nm

(s-*trans*,s-*cis*)

E-5.86 kcal mol⁻¹
λ_{max}=732nm

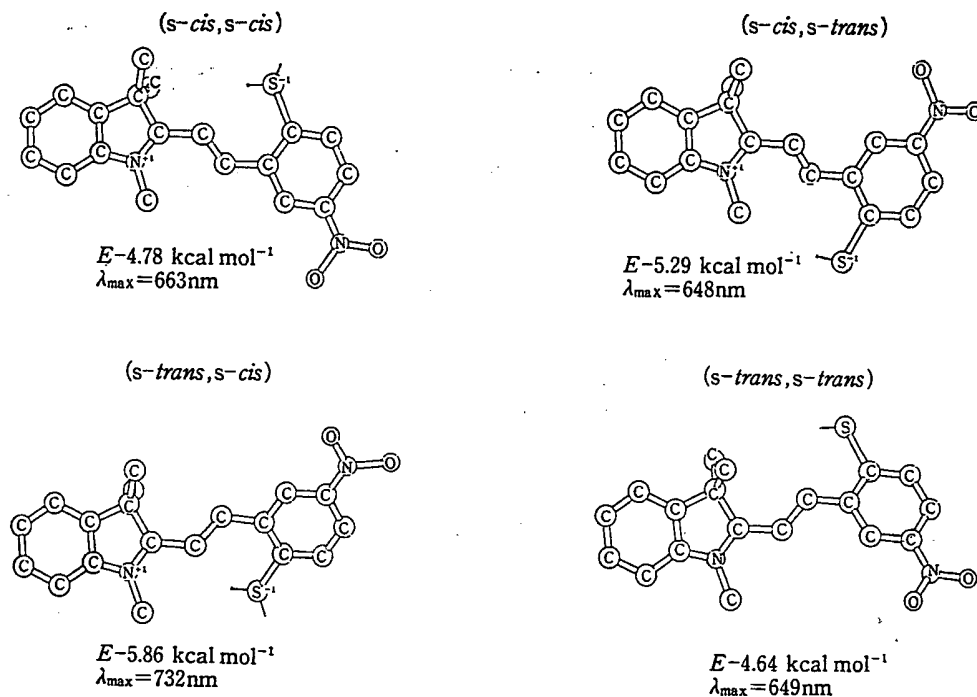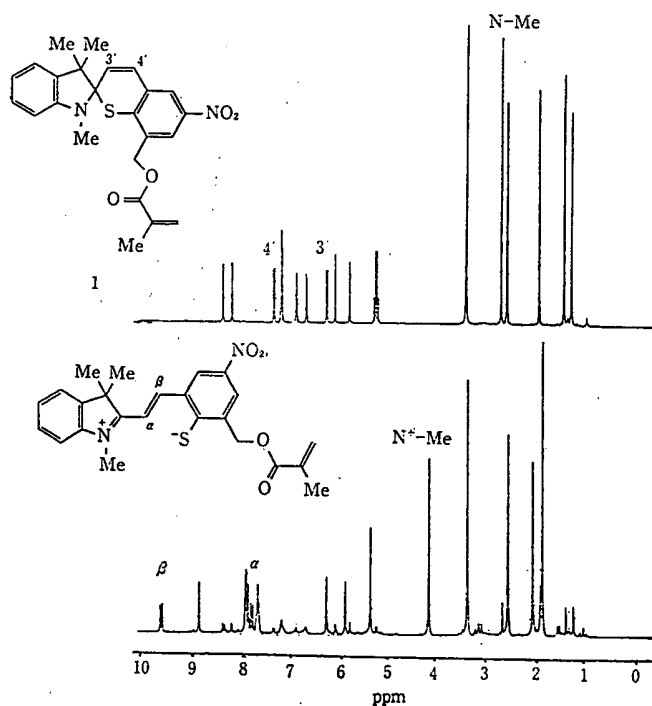(s-*trans*,s-*trans*)

E-4.64 kcal mol⁻¹
λ_{max}=649nm

図5　スピロベンゾチオピラン1の4つの着色種異性体. 安定性と ZINDO 法により
得られた最大吸収波長の計算値.

　一方，中村らは，スピロピランおよびスピロオキサジンのフォトクロミック特性の違いに注目
し，それらの相違点を明らかにすべく分子軌道計算を行い，とくに開環発色型の最適構造を
MNDO 法を用いて推定した．さらに，INDO/S-CI により閉環型無色種と開環型発色種の最大
吸収波長を理論計算し，実測値とよい一致をみている[9]．

A

1.4　光骨格変換反応による準安定系フォトメロシアニン着色種の溶液および結晶構造

上記で述べた種々のスピロベンゾチオピランの不安定型着色種 1_{MC} の溶液構造は，低温下での NMR （^{1}H, NOISY 法，^{13}C, ^{1}H–^{1}H COSY 法）測定および同位体ラベル実験により検討した[4]．

図 6 に，スピロベンゾチオピラン [1, R_1=CH$_2$OCO(Me)=CH$_2$, R_2=Me, R_3=H] の閉環無色種と開環着色種を含む溶液の NMR データを示した．

着色種の ^{1}H-NMR において，N位–メチル基に帰属されるケミカルシフト値が閉環スピロ構造のそれよりも 2 ppm 程度低磁場シフトしており N 原子が cationic であることが示唆される．さらに開環構造における C_α=C_β 間のビシナル–H カップリング値が 15 Hz と *trans*-構造を支持していることと電子スペクトルにおける着色種の吸収極大値 （λ_{max}） が溶媒極性の影響を大きく受けることなどを考慮すると，着色種の溶液構造 1_{MC} は *trans*-zwitterionic 型構造と結論される[4]．

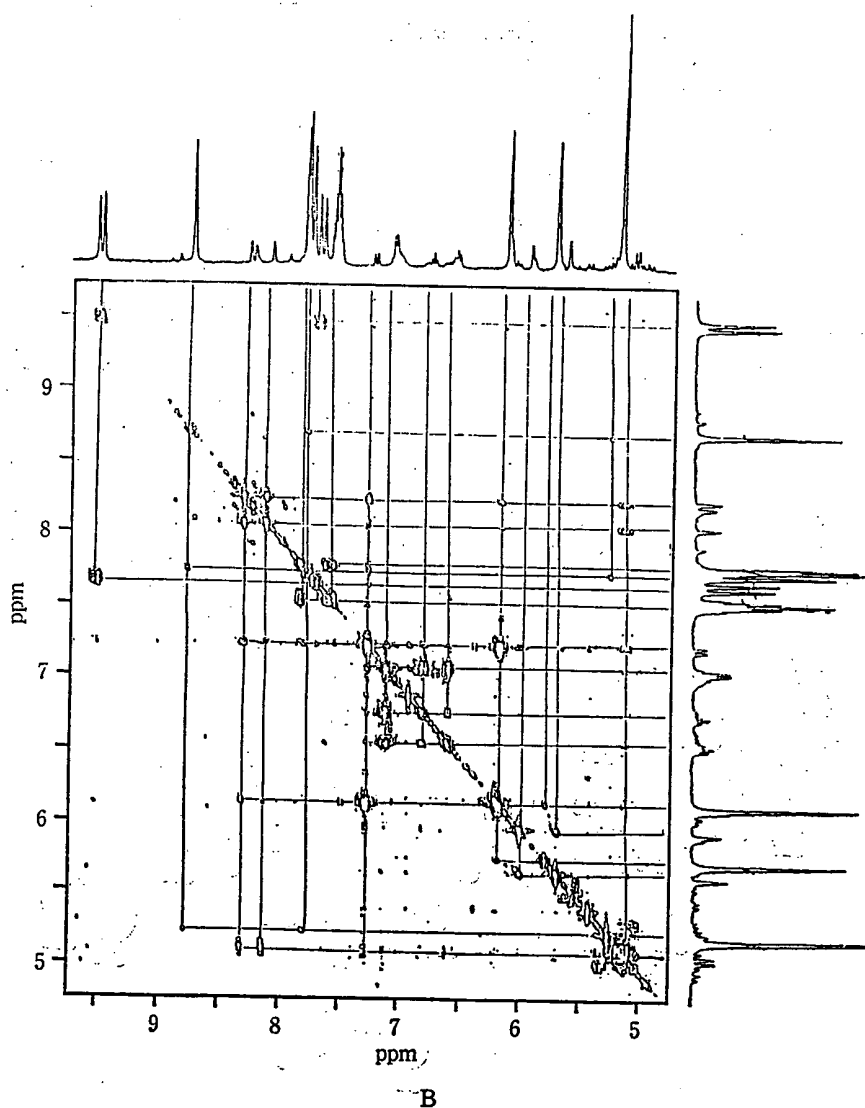一方，安定なスピロ体 1_{SP} における N–Me は ^{1}H-NMR において 2～3 ppm にシャープなシグナルを与え，また開環構造 zwitterion 型では 4～5 ppm に独立なシグナルを与えることか
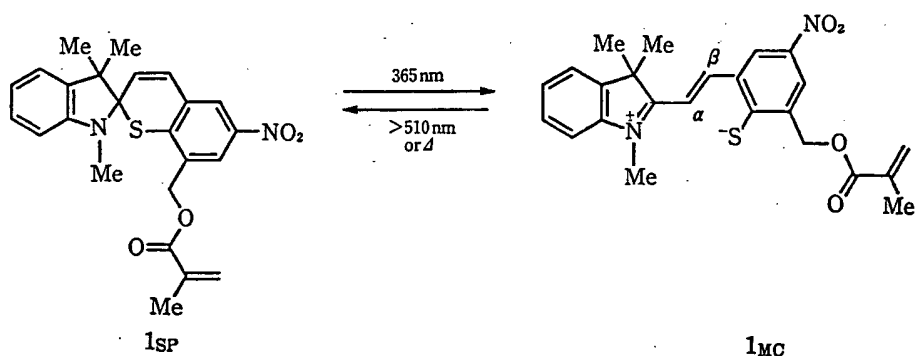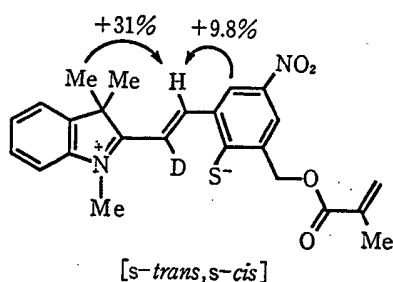

図 6　1 の DMSO-d_6 中での ^{1}H–^{1}H COSY.

58

図 7

[s-*trans*, s-*cis*]

図 8 スピロベンゾチオピラン着色種の ^{1}H-NMR における
NOE 効果.

ら，これらの積分値より消色-着色種間の見かけの暗熱平衡定数 (K_{eq}) が算出される．R_3 にメタ
クリロキシメチル基のような嵩高い置換基がある場合，室温では大きく着色型に平衡が偏った．
また，NMR における NOE 実験および sp^2-C$_\alpha$ 炭素の選択的重水素化によるスペクトルの比較
により，その溶液構造 1_{MC} は (s-*trans*, s-*cis*)-zwitterion 型と結論される[4]．

　多くの有機フォトクロミック化合物の着色構造体は，溶液中では不安定なものが多く，とくに
スピロピラン類は上述のようにその寿命は数秒以下である．筆者らはこれら不安定な着色種の結
晶構造を解明すべく単結晶の単離を試みた．その結果，スピロベンゾチオピランの紫外光照射に
より生成したフォトメロシアニンの深緑色溶液から深青色針状結晶を比較的収率よく得ることに
成功した[10]．それらX線結晶解析の結果を図9の ORTEP 図に示した．得られたフォトメロシ
アニン結晶は，予想に反し (s-*trans*, s-*trans*) 型構造であり，DMSO 溶液中での構造 (s-
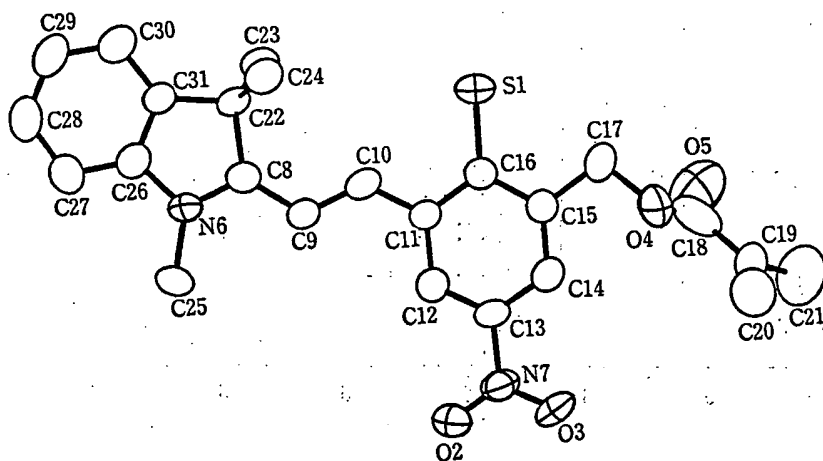

図 9

trans, s-cis）とは明らかに別の異性体構造をとっていた.

　興味深いことに，これら各原子間の結合距離を検討した結果，これらフォトメロシアニンはチオケトン-アシニトロ型分子構造をとっていることが示唆され，これら結晶のIRスペクトル解析の結果もこれを支持している. また，単位セル中（$Z=4$）でこれらの結晶は，H-型スタッキング構造を形成しており大変ユニークな結晶構造を有していることがわかった[11].
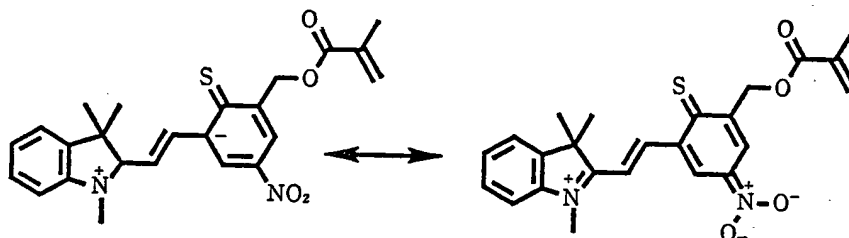

図 10
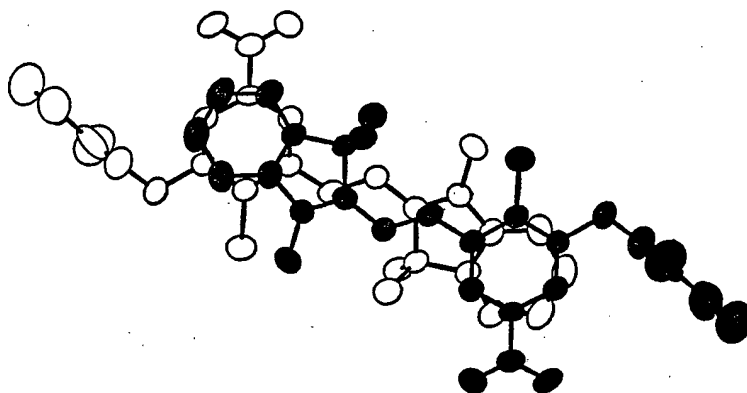
図 11　スピロベンゾチオピラン 1 のフォトメロシアニン H-型スタッキング構造.

　これら深青色結晶は，メタノールに溶解すると直ちに濃緑色溶液（λ_{max}, 673 nm）を与え，（*s-trans, s-cis*）型構造の着色種を生成した.

1.5　スピロベンゾチオピラン溶液の UV 照射により生成する擬結晶[10]

　スピロベンゾチオピラン 1 の UV 照射により生成する zwitterionic 型着色種は，溶液中では熱的に不安定であり室温において直ちに消色する. しかし，1 のヘキサン溶液（淡黄色）に室温で UV（365 nm）を照射し続けるとガラス容器内壁に橙色結晶が徐々に析出する. この結晶を暗所下で極性溶媒に溶解させると直ちに深緑色に着色し，（*s-trans, s-cis*）-zwitterion 型着色種を与えた. また，この橙色結晶はピエゾクロミズムを示し，結晶すり潰しにより緑色に着色する.

　また，この橙色結晶を $-50℃$ でアセトン-d_6 に溶解させ，$-40℃$ にて NMR を測定したところ溶解初期においてはスピロ型(A)と開環型(B)に帰属されるシグナルが観測され，それらの積分値からA：Bは 1：1 であった. しかし，この相対比は $-40℃$ においても経時変化し7時間後においては 3：1（A：B）の平衡値に達した. これらのことから生成した橙色結晶は，A_nB_m 型会合体と推測されるが，それら微結晶の電子スペクトル（透過法）は 1 の閉環スピロ型のスペクトルと有意な差が認められず詳しい分子構造については結晶構造解析などによる検討が必要である.
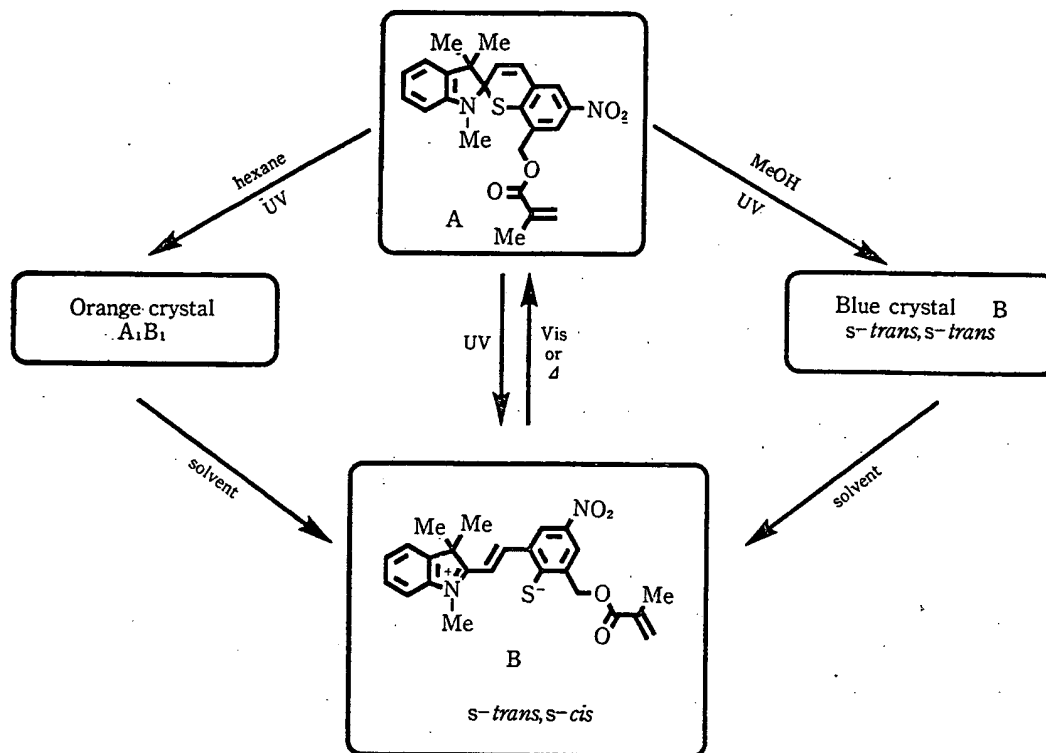
図 12　スピロベンゾチオピラン 1 からの擬結晶生成.

1.6　スピロベンゾチオピラン基を側鎖とするフォトクロミックポリマー
——不安定フォトメロシアニン着色種の長期安定化

スピロベンゾピランを側鎖とするフォトクロミックポリマーは，側鎖の光骨格変換反応によって誘起される高分子物性の光制御という観点から大変興味がもたれており，入江，Smets らによって興味深い研究報告がなされている[12]．本節では，筆者らが開発したスピロベンゾチオピランを側鎖とするフォトクロミックポリマーの合成と光特性について紹介し，次節では，Se-スピロベンゾピランを含む逆フォトクロミックポリマーの合成と光特性について述べる．

8′ 位にメタクリロキシメチル基を有するスピロベンゾチオピラン 1 は，MMA またはスチレンとのラジカル共重合によりスピロベンゾチオピラン含有量（0.5～32%）の異なったフォトクロミックポリマー 2(M_w：4～10×10⁴) を収率よく与える．また，PhMgBr を開始剤とする 1c と

1
a,　R=Me
b,　R=CHMe₂
c,　R=C₁₈H₃₇

2
a,　R=Me
b,　R=CHMe₂
c,　R=C₁₈H₃₇
d,　R=C₁₈H₃₇, isotactic
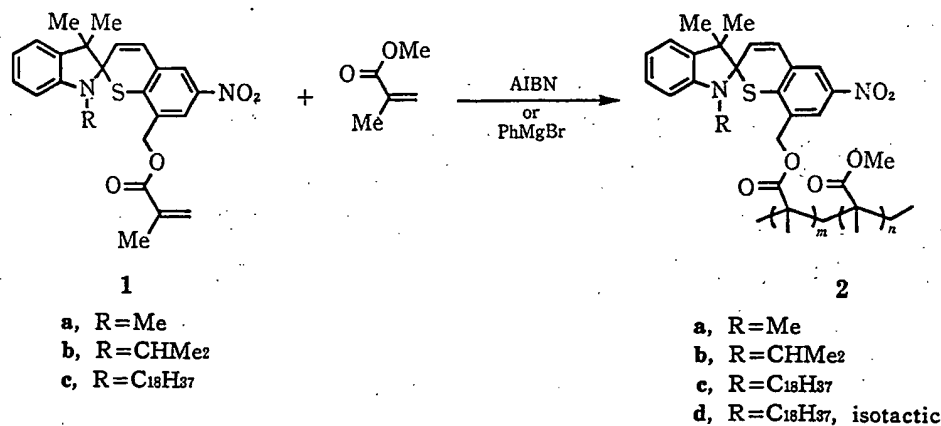
MMA のアニオン共重合によりアイソタクチックポリマー（**2d**，スピロピラン含有量 5.4%，95% アイソタクチック）も合成し，官能基の立体配向によるフォトクロミズムへの影響もあわせて検討した[13]．

light yellow   green
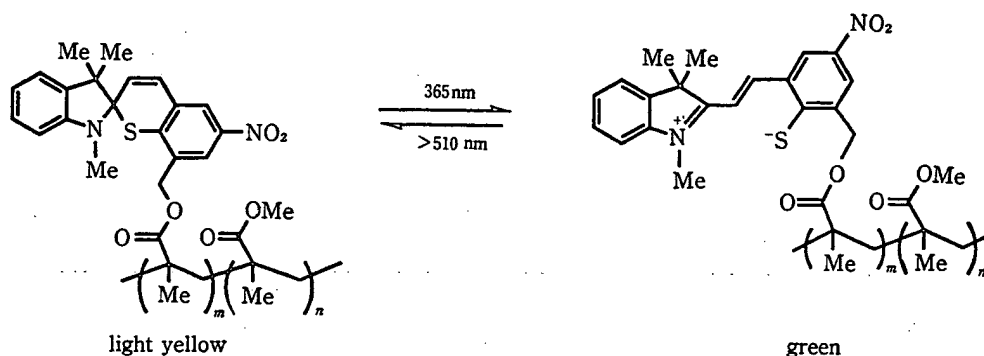
図 13

　得られた淡黄色ポリマーは，溶液中，紫外光照射（365 nm）により直ちに濃緑色に着色し，表1に示した半減期で徐々に退色する．これらの吸収極大波長（λ_{max}）は，N位-置換基の種類を換えても変化しない．一方，これらをキャスト法により薄膜にし（キャストフィルム，膜厚＝〜0.3 mm），これらに紫外光を照射（365 nm）すると淡黄色フィルムは直ちに濃緑色に着色し，その吸収末端は GaAs 半導体レーザー波長域の 900 nm 付近まで達する．

　大変興味深いことに，この濃緑色着色フィルムは室温暗所下においてまったく消色することなく長期にわたって固定化され，その吸光係数は 4 年以上にわたって変化していない．この不安定着色種の固定化率は N 位-置換基の種類により大きく変化し，とくに，長鎖アルキルのオクタデシル基（**2c**）を導入すると着色種の安定性は大幅に増大し，その安定性はモノマーに比べて約 320 万倍以上増加した[13]．一方，アイソタクチック PMMA 型のフィルム（**2d**）は，それらエステル基の配向効果はみられず，むしろ準安定系着色種の固定化率は低下した．緑色に着色したキャストフィルムは，可視光（>510 nm）照射または加熱（>80℃）により速やかに消色する．

　アルゴン下でのフォトン-フォトン・モード（500 W 超高圧水銀灯）による着色-消色繰り返しサイクルは，約 100 回程度（初期吸光度の 50% まで退色）であった．しかし，**1**を PMMA 中に混合したのみのコンポジットフィルム（**1c**, 4.2%）は，室温においてその発色種は固定化されることなく暗所下においても徐々に

図 14 フォトクロミックポリマー **2c**, キャストフィルムの着色種固定化．実線は，フィルムを紫外光照射直後と 10 分間隔で記録した電子スペクトル．破線は，さらに可視光照射した後の電子スペクトル．

表 1　フォトクロミックポリマー 2 の溶液中およびキャストフィルムでの最大吸収波長と半減期

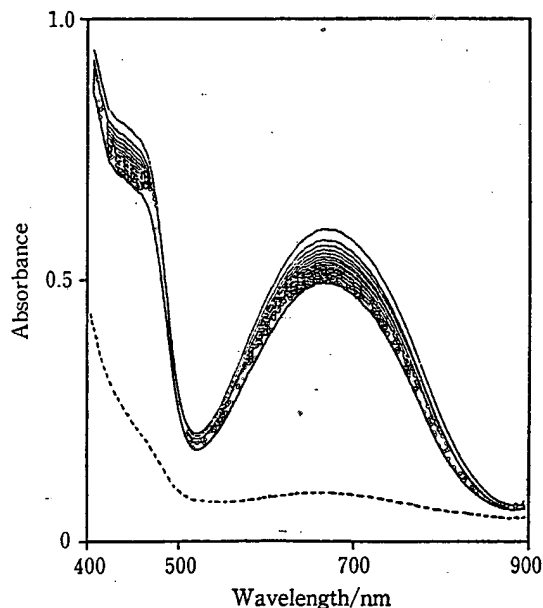| Polymers[a]	λ_{max}/nm			
	Acetone	$(\tau_{1/2}/min)$[b]	Film[c]	(Fixation/%)[d]
2 a	659	(0.39)	671	(35)
2 b	652	(0.98)	677	(29)
2 c	655	(0.86)	665	(79)
2 d[e]	655	(0.83)	659	(38)
2 e[f]	—	(—)	715	(11)
composite **1 c**[g]			680	(14)

a) SP content, in a range of 2.2-5.6 mol% (elementary analysis); M_w of copolymer, 4.9-8.5×10⁴ (by GPC, polystyrene standard). b) Half life of metastable colorless form in acetone at 25°C. c) Film thickness was determined as ∼300 mm by analyzing an interference fringe in IR spectrum. d) Fixation rates of the metastable colored form were obtained by the following equation : $[(A_{12}-A.)/(A_0-A.)] \times 100$, where $A.$ is absorbance at the initial state before UV light irradiation, while A_0 and A_{12} represent absorbances at $t=0$ h and 12 h, respectively, at 26°C after irradiating with UV light. e) Tacticity of 92% (mmmm) was determined by ¹H-NMR[5]. f) SP-styrene copolymer, prepared by radical polymerization. g) Cast film of PMMA composite doped with 1c in 4.2%.

退色した．この原因を理解するため準安定型着色フィルムの熱退色における動力学的検討を行った．図 15 には **2c** の熱退色速度定数の 1 次プロットを示した．側鎖型ポリマーはコンポジット型と違ってその着色系熱退色速度の 1 次プロットに明白な屈曲点がみられ，それら熱退色がPMMA の主鎖の局所モード緩和に由来するものと理解される[14]．一方，**1c** のコンポジットフィルムでは，図 16 に示したように均一溶液中での通常の直線関係と同様の結果が得られた．
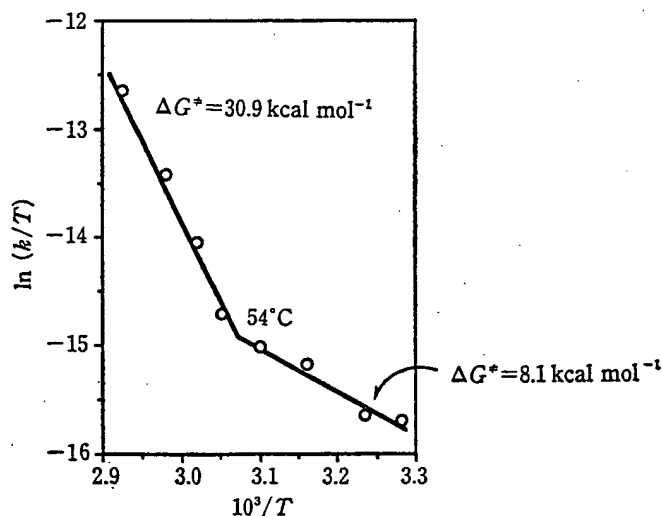
図 15　フォトクロミックポリマー **2c** の着色種熱退色 1 次プロット．

図 17 に，コポリマー着色フィルム **2c** の熱退色状況の長期にわたる経時変化を示した．初期における若干の熱退色の後，長期にわたって着色種の吸光係数に顕著な変化がみられないことがわかる．

$$\Delta G^* = 24.3 \text{ kcal mol}^{-1}$$
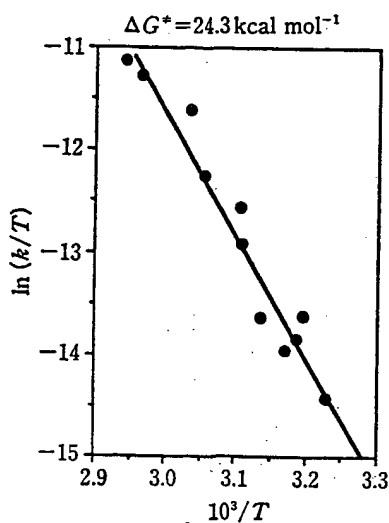
図 16　スピロベンゾチオピラン **1c** の PMMA コンポジットフィルムの着色種熱退色1次プロット.
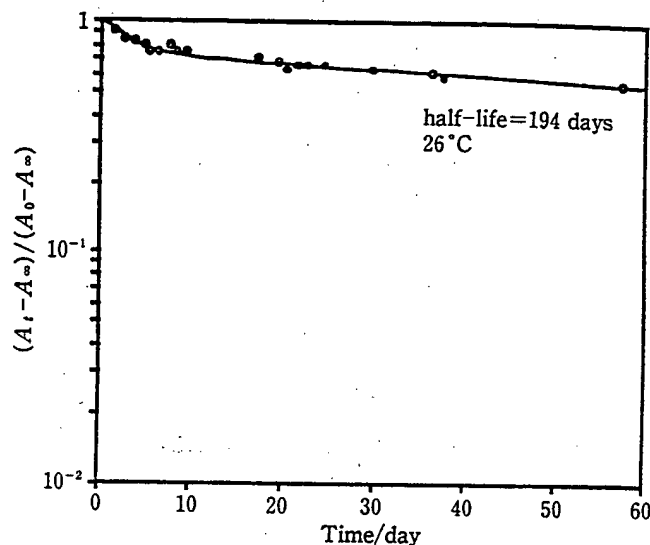
図 17　フォトクロミックポリマー **2c** の長期熱安定性.

2　Se-スピロベンゾピランと逆フォトクロミズム[15]

2.1　スピロセレナゾリノベンゾピランの合成

Y＝O, S
R_1＝CH＝CH$_2$,　CH$_2$OCOC(Me)＝CH$_2$
　　　CH$_2$OCOC$_{21}$H$_{43}$
R_2＝Me, *i*-Pr, C$_{18}$H$_{37}$
R_3＝H, Me, OMe

3
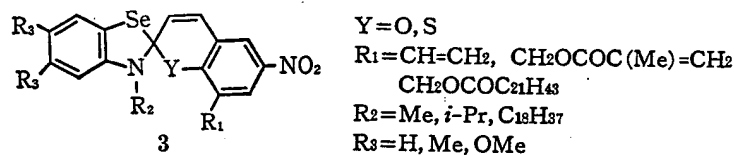
図 18

　スピロセレナゾリノベンゾピラン **3** は，**1** と同様に一般的なスピロピラン合成法とその応用により収率よく得られ，NMR, IR, Mass などのスペクトル分析および元素分析により同定された．1例として 8-ビニル-Se-スピロピランの合成ルートを以下にまとめた.

図 19

64
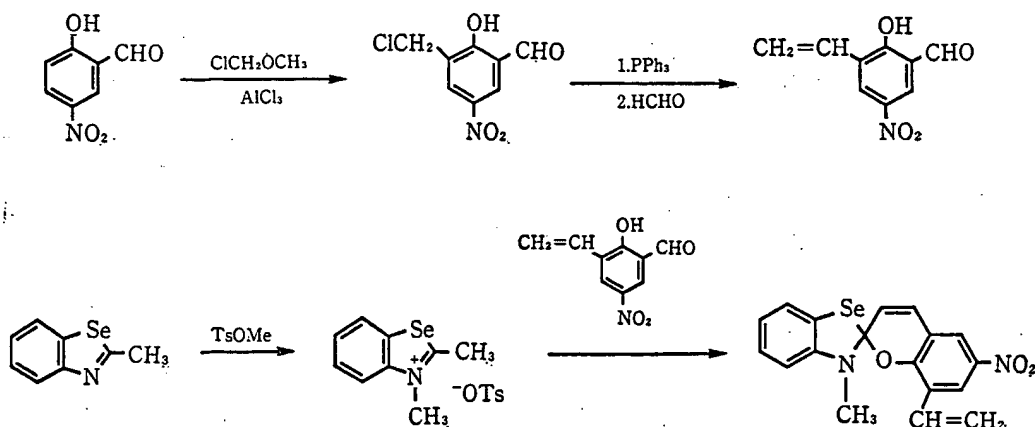
芳香環上やN位の置換基の種類に無関係にいずれも逆フォトクロミズムを示す. **3**は溶液中において青～青紫色 (λ_{max}=550～600 nm) に着色し, 図 21 の表にまとめたようにこれらのモル吸光係数は 2～8×10^4 と他のスピロピラン類に比べても際だって大きな値を有している.

これらの溶液は, 可視光 (>510 nm) 照射により直ちに消色し, また室温暗所下において徐々にもとの青～青紫色に着色した. この消色型の熱安定性は溶媒極性の影響を大きく受け, DMSO などの極性溶媒中ではスピロ型閉環構造が比較的安定であった.
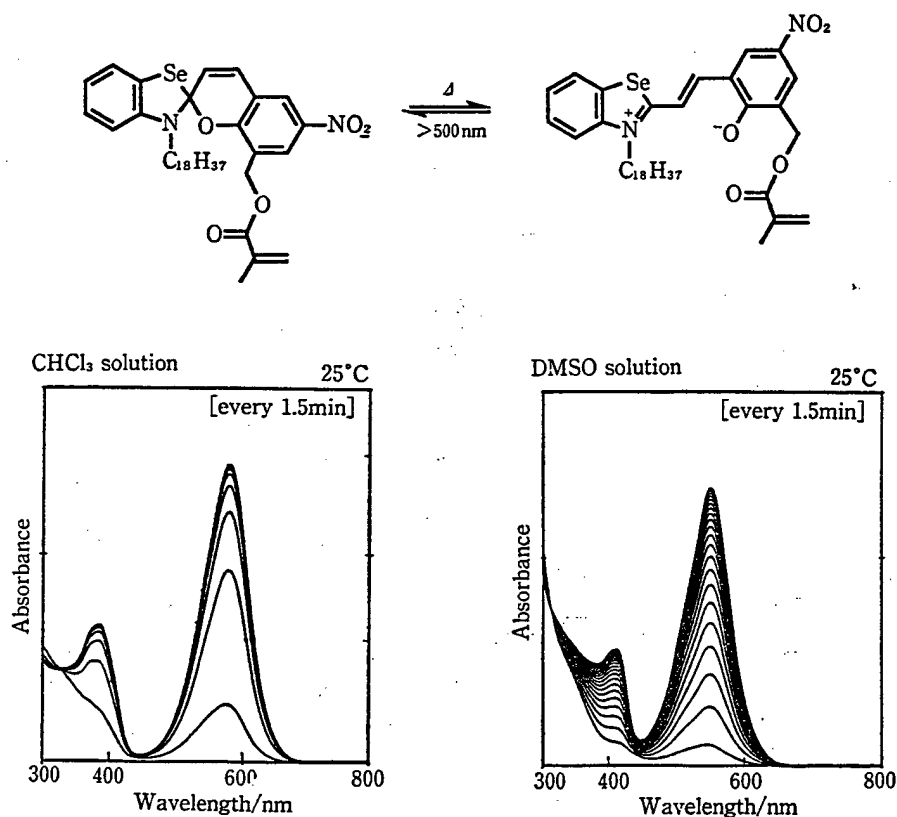
図 20

3の着色種の構造は, R_1 がメタクリロキシメチル基である場合, 室温でほぼ 100% zwitterion 構造をとっており, R_1 が無置換の場合スピロ型と開環構造 zwitterion 型の混合物になった (後述). **3**は優れたフォトクロミック特性を示し, DMSO 溶媒中, P-T モードでの着色-消色の繰り返しは 3000 回を超えた. 図 22 にその様子を R_1=ビニルの例について示した.

しかし, **3**は, クロロホルムなどのハロゲン化溶媒中ではフォトクロミズムの繰り返し特性は低く, 300 回ほどの着色-消色のサイクルで分解する. 分解物は, NMR, Mass 分析によりハロゲン付加体であることが確認されている.

2.2 スピロベンゾセレナゾリノナフトオキサジンの合成と正・逆フォトクロミズム

筆者らは最近, スピロナフトオキサジン類の優れた繰り返し耐久性に着目し, 1-位に Se 原子を含む種々のスピロナフトオキサジン誘導体を新規に合成し, それらのフォトクロミック特性を検討した[16].

a : R¹, R² = H
b : R¹ = H, R² = CH₃
c : R¹ = H, R² = OCH₃
d : R¹, R² = OCH₃
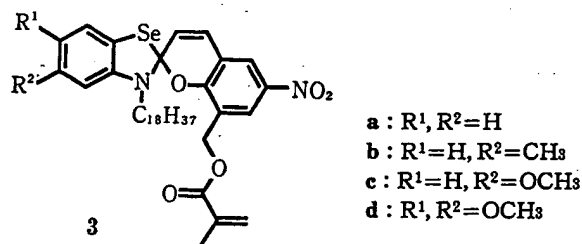
	In CHCl₃			In DMSO		
	λ_{max} nm	$\varepsilon \times 10^{-4}$ M⁻¹cm⁻¹	$\tau_{1/2}$[a] min	λ_{max} nm	$\varepsilon \times 10^{-4}$ M⁻¹cm⁻¹	$\tau_{1/2}$[a] min
3a	578	5.0	2.0	547	4.3	4.0
3b	580	4.9	1.9	550	4.1	4.8
3c	586	4.6	2.5	557	3.8	4.3
3d	583	5.5	2.6	555	4.7	5.6

a) Half life of the metastable colorless spiro-form of 3 at 25°C.

図 21

R = H, CH₃, OCH₃　　　in DMSO

R=H (λ_{max}=562 nm)　　　R=CH₃ (λ_{max}=565 nm)　　　R=OCH₃ (λ_{max}=570 nm)
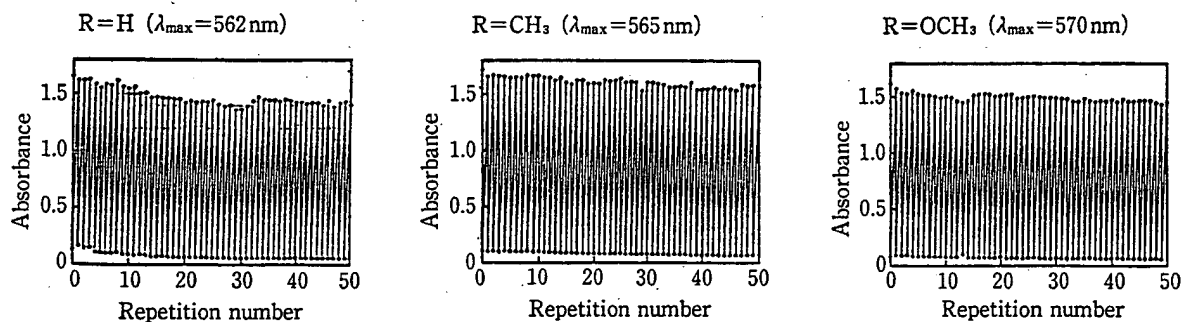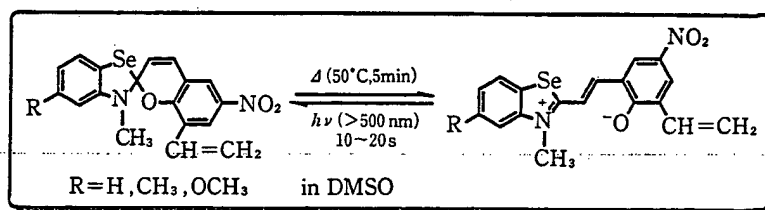
図 22

　スピロベンゾセレナゾリノナフトオキサジン 4 は，ベンゾセレナゾールとニトロソナフトールとの縮合反応により収率よく合成できる．興味深いことに，4 は使用する溶媒の極性により正フォトクロミズムおよび逆フォトクロミズムを示す．すなわち，アルコールなどの極性溶媒中では濃緑色を呈し，着色種がメロシアニンの安定な逆フォトクロミズムを示した．これらの吸収極大値（λ_{max}）は置換基 R の種類に影響されず 630 nm 付近に現れる．一方，ベンゼンや酢酸エチルなどの非極性溶媒中では淡黄色溶液となり，紫外光照射により濃緑色を呈し正フォトクロミズムを示す．図 23 の表にまとめたように，着色種に由来する吸収極大は R 置換基に無関係に 630 nm 付近であり着色種の λ_{max} は溶媒極性により変化しない．しかし，アセトン，塩化メチレンなどの適度な極性を有する溶媒中では淡緑色を呈し，それらはスピロ型とメロシアニン型の熱平衡状態にあることを示唆している[17]．可視光照射により淡黄色になり，一方，紫外光照射により濃緑

色を呈した. 以下の図表に示したように, アルコール中では平衡は完全に開環着色種側に寄り, またベンゼンなどの非極性溶媒中では閉環スピロ型が安定になった.

一方, アセトンや塩化メチレン中では, 平衡定数が1に近い値を示した.
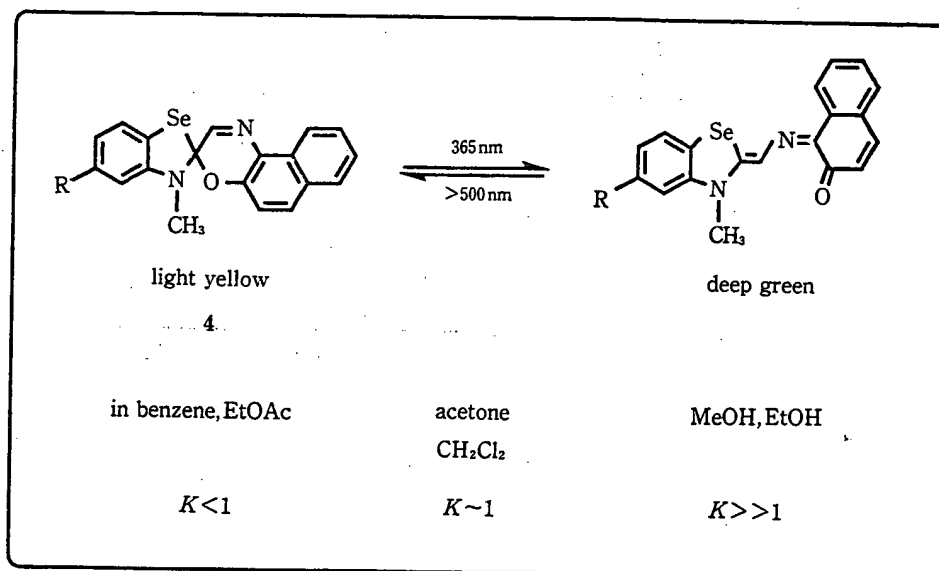
| | Solvent (λ_{max}/nm) | | | | |
	MeOH	Me₂CO	CH₂Cl₂	CH₃CO₂Et	PhH
R = H	625	625	630	625	630
CH₃	630	627	633	625	630
CH₃O	635	636	645	635	640

25°C

図 23

2.3 Se-スピロピランおよび Se-スピロナフトオキサジン類の着色種溶液構造

上記で述べた種々のスピロピラン関連化合物の準安定型溶液構造を低温下での NMR (¹H, NOE 法, ¹³C, 2 次元法) 測定により検討し, さらに消色-着色種間の暗熱平衡定数評価を行った[15]. その結果, Se-スピロピラン 3 はそれら着色種の λ_{max} が溶媒極性の影響を大きく受けることおよびその ¹H-NMR において N 位-メチル基のケミカルシフト値が 2 ppm ほど低磁場シフトしN原子が cationic であること, さらに開環構造における $C_\alpha = C_\beta$ 間のビシナル-H カップリングが 15 Hz と *trans*-構造を支持していることなどがわかった. また, NMR における NOE 実験および α-位の選択的D化によるスペクトルの比較などにより, 着色種の構造は (*s-trans, s-cis*) 型 zwitterion 構造であると結論した.
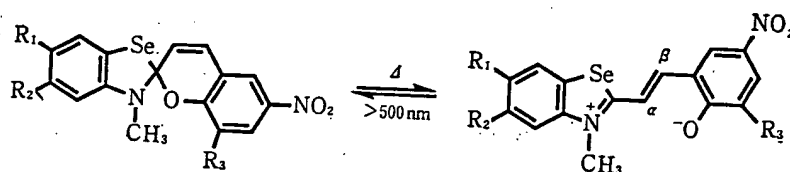
図 24

　一方，**3** のスピロ体における N-Me は，¹H-NMR において 2〜3 ppm にシャープなシグナルを与え，また開環構造 zwitterion 型では 4〜5 ppm に独立なシグナルを与えることから，これらの積分値より見かけの平衡定数（K_{eq}）が算出される．表2に NMR より算出された K_{eq} 値をまとめた．

表 2

R₁	R₂	R₃	K_{eq} (25℃)	N⁺-Me ppm	³$J_{H_\alpha - H_\beta}$ Hz
H	H	H	1.3	4.10	14.4
H	OMe	H	0.67	4.23	15.5
H	Me	H	0.67	4.06	14.7
H	H	CH₂OCOC(Me)=CH₂	10	4.11	14.5
H	OMe	CH₂OCOC(Me)=CH₂	12	4.09	14.6
H	Me	CH₂OCOC(Me)=CH₂	13	4.08	14.5
OMe	OMe	CH₂OCOC(Me)=CH₂	>99	4.41	13.8

　R_3 にメタクリロキシメチル基のような嵩高い置換基がある場合，室温では大きく着色型に平衡が偏った．

　一方，逆フォトクロミズムを示すスピロセレナゾリノナフトオキサジン **4** は，それら着色種の吸収極大値（λ_{max}）が溶媒極性にまったく依存しないことから通常のスピロナフトオキサジンの着色種と同様にケト型中性構造であることが示唆される．このことは ¹H-NMR により支持される．すなわち，**4** のベンゼン-d_6 溶液は無色であり，N-Me に帰属されるシグナルは 2.69 ppm に現れ，スピロピラン閉環体 **1** と同様に N 原子は中性3価である．一方，**4** のクロロホルム-d 溶液は濃緑色に着色しており，その NMR では N-Me は 3.17 ppm に現れ3価原子に結合する Me シグナルに比べ，やや低磁場シフトを示したものの Se-スピロピラン **2** の着色種ほどの大きなシフトを示さなかったことから，**4** の溶液中における着色構造はケト型中性構造と結論される．このとき，スピロ型閉環構造に由来する N-Me のシグナルは観測されなかったことより平衡はほぼ完全に開環着色型に偏っていると考えられる．

2.4　スピロセレナゾリノベンゾピラン基を側鎖に有する新規な逆フォトクロミックポリマー[18]

　3 は，MMA またはスチレンとのラジカル共重合により青〜青紫色のポリマー（M_w：2〜5×10⁴）を高収率で与える．キャスト法またはスピンコート法によって得られた青色フィルムは可視光（>500 nm）照射により消色し，この消色系が長期間安定に固定化された．とくに，本系においても N 置換基として長鎖アルキル基を導入した場合，準安定型無色種の固定化率（87%）・半減期（80 日以上）とも大幅に改善され，その安定性はモノマーの約5万倍以上に達した．これもチオピランポリマーと同様にキャストフィルムの動力学的検討を加えた結果，Se-スピロピランの側鎖型ポリマーはコンポジット型と違ってその準安定無色系熱着色速度の1次プロットに明白な屈曲点がみられたことから，それら熱着色過程が PMMA 主鎖の局所モード緩和に由来するも

のと理解される．一方，**3** のコンポジットフィルムでは，均一溶液中での通常の直線関係と同様の結果が得られた．
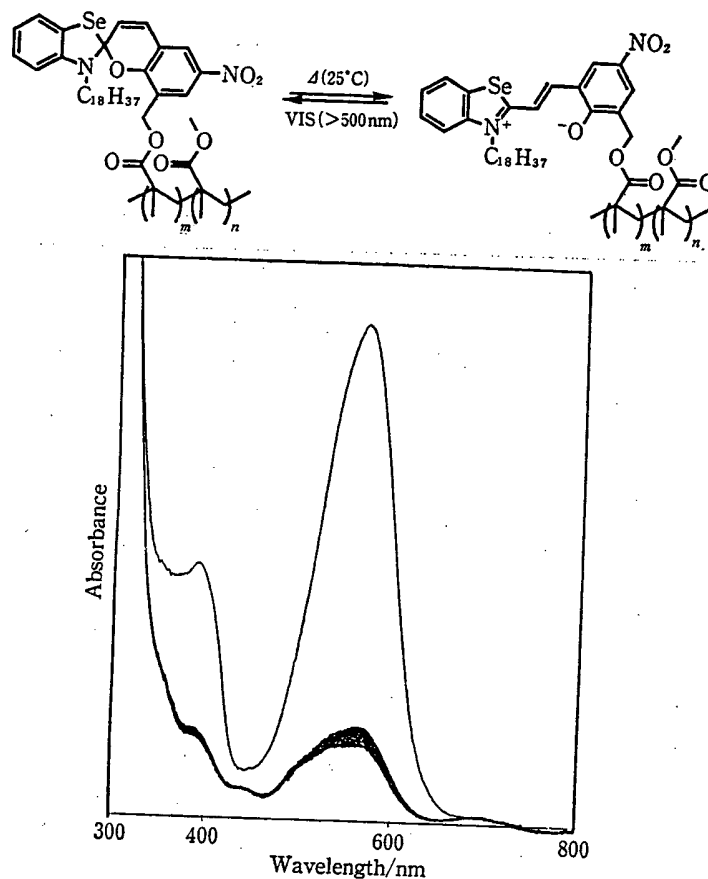
図 25

　一方，**3**(N-$C_{18}H_{37}$, 8′-$CH_2COC[Me]=CH_2$) は，エチルメタクリレートやブチルメタクリレートなどのガラス転移温度の低い高分子主鎖に取り込まれるとキャストフィルム作製過程において *H*-および *J*-会合体を形成し，前者では吸収極大値（λ_{max}）は 450 nm 付近に新たな吸収帯を与え，一方，後者はその吸収極大値（λ_{max}）が 650 nm 付近にシャープな吸収を与えた[18,19]．また，**3**(N-$C_{18}H_{37}$, 8′-$CH_2COC_{21}H_{43}$) の 2 本鎖長鎖アルキル基を有する Se-スピロピランは高分子母体中で *H*-会合体を形成[20]するが，それらの LB 膜は，*J*-会合体形成による興味深いフォトクロミック現象を示した[21]．

　スピロピラン系フォトクロミック化合物は，現象論的な光反応が見かけ上単純であるにもかかわらず，より卓越した光機能を付与すべくそれら化合物の分子設計やそれら光反応に関わる分子化学的な研究アプローチを図ると大変奥が深い．最近，筆者らは光学活性スピロピラン類の合成やこれらの誘導体を配位子とする数多くの遷移金属錯体の合成とそれら新しい光機能の研究展開を行い，いくつかの興味深い現象を見いだしている．このように，スピロピランは，眺める角度・方向を変えてみると，その応用性と発展拡張性があり，さらには，新しい機能発現の開拓という観点ではまだまだ多くの潜在性のある大変魅力的な光機能性化合物である．今後ますます関

連する研究分野が活発になるものと期待される.

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ABSTRACTS

Chemistry of organic photochromism

1. Introductory remarks

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History of photochromism was briefly surveyed. The active research almost ceased in the end of 1960 because of failure in synthesizing fatigue resistant compounds. Remarkable progress in opto-electronic technologies revived the interests of photochromism in the beginning of 1980. The recent efforts were focused in development of photochromic compounds for light limiting glasses, optical memory media, and photo-optical switching devices. The present state of the art was reviewed.

2. Molecular orbital studies on photochromic molecules

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Ab-initio and semiempirical MO studies on organic photochromic molecules are reviewed. An understanding of the systems in terms of electronic structure is presented, focusing on four important requisites of photochromism: absorption property, thermal stability, reaction mechanism, and wavelength effect.

3. Physical chemistry of photochromism. Photocyclization mechanism of *cis*-stilbene analogues

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Recent progress of photocyclization mechanism of stilbene analogues, especially diphenylcycloalkenes, was reviewed from both theoretical and experimental points of view. The time dependent analysis of the primary processes based on theoretical calculations and laser photolysis methods successfully revealed the details of the reaction mechanism.

4. Spiropyrans

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Spiropyrans being one of the most typical organic photochromic compounds have featured in recent research interests in photo-functional materials such as photoinformation memories and optical recording. In this article, detailed structural study relevant to photochromism of spiropyrans and stabilization of their metastable merocyanine form are described, while synthesis and optical properties of novel negative Se-spiropyran derivatives are summarized. The structures of the metastable colored-form of the photochromic spirobenzothiopyrans were determined to be the zwitterionic form having (*s-trans, s-cis*) conformation in solutions, although X-ray crystallographical analysis of these colored-merocyanins suggested to be the zwitterionic (*s-trans, s-trans*) form with H-type stacking structure in crystals. Diode-laser susceptible photochromic poly(methylmethacrylate) anchoring spirobenzothiopyrans as side group are prepared by radical copolymerization of a series of spirobenzothiopyrans having methylmetacryloxy group with MMA. The cast films of colorless SP-MMA copolymers immediately colored to deep green by being exposed to UV light. The resulting colored film retained the deep green color in the dark over a year after initial slight decoloration, whereas the monomers in the composite film in PMMA matrix bleached slowly even at room temperature. The stable colored form of spirobenzoselenazolinobenzopyrans which showed negative photochromism, were determined to be the zwitterionic (*s-trans, s-cis*) structure in solutions, while photochromic properties of the related spirobenzoselenazolinonaphtooxiazin were largely affected by solvent polarity. A series of novel negative photochromic PMMA having Se-spiropyrans as side chain showed their reversible photochemical color change: visible light irradiation inducing rapid color-change from purple to colorless. This metastable colorless spiro-form was fixed more than 100 days in the dark, although the composite-film of PMMA doped with Se-spiropyran bleached back to the stable colored merocyanine-film.

5. Spirooxazines

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Spirooxazines are the photochromic compounds that have excellent fatigue-resistant property. Their colorless forms turned to colored forms by ultraviolet-light irradiation. Colored forms turned to the colorless forms either by heat or visible-light irradiation. These photochromic phenomena occur by cleavage and formation of the spiro C-O bond of the oxazine ring. In this article, an outline of photochromic properties of spirooxazines (coloring and bleaching rate, color density, thermal stabilization of the colored form, fatigue-resistant property, *etc.*) is described. In particular, (i) spirooxazines have relatively high coloring and bleaching rates: (ii) The molar absorption coefficients of colored forms of spirooxazines are 10^4–10^5 mol^{-1} dm^3 cm^{-1}: (iii) Spirooxazines show almost no fatigue after 2000 coloring and bleaching cycles. Classification of the spirooxazine ring system is given. Spirooxazines have a wide variety of molecular structures with more than 100 ring systems. The relationship between the molecular structure (*i.e.*, degree of conjugation and effect of substituents) and absorption wavelength of the colored form is discussed. In general, spirooxazine compounds having the ring system with longer conjugation absorb longer wavelength light. Photochromic polymers with spirooxazine pendant groups have interesting properties such as high color density and low thermal bleaching rate. Spirooxazines have been practically used as eyeglasses (photochromic lenses) because of their well-balanced properties.

6. Diarylethenes

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The molecular design principle and synthetic methods of thermally irreversible and fatigue resistant photochromic diarylethenes with heterocyclic rings, such as thiophene or benzothiophene, were described. The photo-generated colored forms were thermally stable at 80°C for more than 3 months and the coloration/decoloration cycles could be repeated more 10^4 times with keeping the photochromic performance. The response times of photocyclization and ring-opening reactions were measured to be less than 10 ps by a pico-second laser photolysis method. The color variation of closed-ring forms from yellow to blue was realized by changing the substitution position of the thiophene rings to the ethylenyl moiety and introducing appropriate substituents to the thiophene rings. Gated photochromic reactivity was given to the molecules by introducing intramolecular hydrogen or S-S bond-forming groups.

7. Chemistry of fulgides and related compounds

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Fulgides are considered to be thermally irreversible photochromic compounds. This review article about the fulgides, with 90 references, deals with: (1) History of fulgides in the early times, particularly before they obtained the thermal stability, (2) Effect of steric factor on the photochromism of fulgides, (3) Effect of aromatic rings on the photochromism of fulgides, (4) Structure elucidation and chirality of fulgides, (5) Effect of media on the photochromism of fulgides, (6) Photophysics of photochromism of fulgides, (7) Attempts to apply fulgides to photon-mode rewritable optical memory having non-destructive readout ability, (8) Chemistry of photochromic fulgide derivatives with additional function, (9) Thermally irreversible and reversible photochromic molecules related to fulgides, (10) Synthetic methods of fulgides, (11) Other interesting chemistry of fulgides. The time of the second generation of fulgides, just having thermal irreversibility, is coming to an end, and the time of the third generation of fulgides, with additional functional properties, has just commenced. Photofunctional molecules, expected to play important roles throughout the coming "Era of Photonics", will come out from the research in this field.

8. Cyclophanes

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The cyclophanes, in which the reactive aromatic rings are fixed in the suitable positions by the bridged chains, are expected to be good photochromic compounds. The cyclophanes containing anthracene rings (so-called *Anthracenophanes*) and *Metacyclophanes* are known to show photochromism. The main members of the *Anthracenophanes* are anthracenophanes (having two anthracene rings), anthracenonaphthalenophanes (having an anthracene ring and a naphthalene ring) and anthracenoparacyclophanes (having an anthracene ring and benzene ring). Photoirradiations of these orange or yellow *Anthracenophanes* give colorless intramolecular cycloadducts. These photoproducts revert to the original cyclophanes by heating or irradiation at shorter wavelength. These colorless species are generally stable at room temperature. Substituents on the bridged chains or the aromatic ring affect the reactivities of the *Anthracenophanes*. The members of the *Metacyclophanes* are colorless [2.2]metacyclophane-1-enes and [2.2]metacyclophane-4,9-dienes, which show photochromism with red tetrahydropyrenes and green dihydropyrenes, respectively. In the case of metacyclophane-enes the cyclophanes are more stable than the hydropyrenes, while in the case of metacyclophane-dienes the hydropyrenes are generally more stable.

9. Photochromism based on the photosensitized oxygenation of polycondensed aromatic compounds

Sumio Tokita *Department of Applied Chemistry, Faculty of Engineering, Saitama University, Urawa, Saitama 338, Japan*

Recent progress in photochromism based on the photosensitized oxygenation of polycondensed aromatic compounds is shortly reviewed. Main topics are as follows: (1) Structural chemistry of strained polycondensed aromatic compounds and their endoperoxides. (2) Position specificity in photosensitized oxygenation of benzo[1,2,3-*kl*:4,5,6-*k'l'*]dixanthene (5a), anthra[1,9-*bc*:4,10-*b'c'*]dichromene (11a), and their analogues. (3) Observed electronic spectra data of benzodixanthenes and anthradichromenes together with the prediction of absorption maxima using molecular orbital techniques.

10. Photochromism of chalcone derivatives

Ryoka Matsushima and Hirotaka Mizuno *Department of Applied Chemistry, Faculty of Engineering, Shizuoka University, Hamamatsu 432, Japan*

As a simplified model of the naturally occurring anthocyanin pigments, synthetic 2-hydroxychalcones with 4'-amino groups undergo facile photochemical conversion into highly colored flavylium ions on irradiation with 365–436 nm light in aqueous ethanol solution in the pH region of 4–6. The colored solutions were substantially stable against prolonged irradiation with visible light. The absorption bands of the flavylium ions around 530–560 nm are strong and well separated from those of the chalcones around 400 nm. Some of the derivatives feature good reversibility for repeated photochemical coloration and thermal reversion without significant fatigue in dilute solution, while some other derivatives feature a high thermal stability. Similar photochemical coloration occurs in many solid polymers, though irreversible thermal bleaching takes place. The photochromic properties are discussed in terms of frontier orbitals.

11. Organic materials for transmittance control

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An overview of materials for transmittance control using the organic photochromic compounds is given. Some of them have already been applied to the ophthalmic lens and sunglass markets. However, even in these applications, the organic photochromic compounds have a disadvantage of lack of stability. The organic photochromic compounds lose their photochromic efficiency gradually as the number of color reversals or the total amount of ultraviolet radiation increases. The photochromic durability requirement for architectural and automobile glazing applications is more stringent. At present, the development of the total technologies for the transmittance control using the organic photochromic compounds is desired to extend this product life for large area of glazing application.

12. Studies on photochromic performance of derivatives of fulgide and application to optical recording materials

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Work on organic photochromic compounds has been attracted much attention because of a high possibility being used as a re-writable recording media. Owing to a highly-thermal fatigue resistant characteristic, a derivative of heterocyclic fulgide has been regarded as an excellent photochromic compound. In this paper, the author reported on a relationship between chemical structure and photochromic performance of fulgide in dilute solution or PMMA thin film and furthermore for practical use a possibility of fulgide disk as a recording media was also mentioned. In absorption spectra properties, it was clarified that an increase in electron-donating ability of heterocyclic or benzilidene structure of fulgide caused a bathochromic shift of the absorption of colored, *e.g.* photocyclized form of fulgide and some of which showed an enough susceptibility at semi-conductor laser oscillation wavelength (780 nm). On the other hand, quantum yield for both coloration and bleaching reaction of fulgides indicated that an increase of an electron-donating ability of the heterocyclic or benzyl structure caused a higher yield for coloration. Thermal stability and cycle fatigue resistance (photochemical stability) of fulgide in PMMA thin film were investigated and it was proved that oxazole structure as a heterocycle of fulgide was effective at improving the both stabilities. An optical fulgide disk was prepared and it was revealed that excellent read-out signal (CNR/49dB) was acquired and a reversible cycle-repeating, *e.g.* recording and erasing was possible.

13. Application of photochromic compounds to multiple optical memory

Junichi HIBINO   *Central Research Laboratories, Matsushita Electric Industrial Co., Ltd., Souraku-gun, Kyoto 619–02, Japan*

Optical memories offer the potential for significant improvements in capacity over conventional mass memory technologies such as disks and magnetic tapes. Recent advances in optical memory technology make it the leading contender for the next generation of mass memory devices. The memory density in optical data storage using lasers can be increased beyond the limit of planar packing of optical bits by multiplying memory location by the frequency domain. In this chapter, we report a new multiple optical memory by the combination of multi-frequency and polarized recording by using the recording medium stacked with the five spiropyran aggregate layers. Investigating the aggregate-forming ability of the new synthesized photochromic spiropyrans, it can be developed novel five kinds of spiropyran aggregates each of which has a sharp absorption band at different wavelength. A recording medium stacked with the aggregate layers is confirmed 10-multiple optical memory by means of combining the multi-frequency recording with the recording by two mutually perpendicular linear-polarized lights. Furthermore the light absorption changes of these aggregates show nonlinear response with a threshold energy for laser irradiation. By using this phenomenon, non-destructive reading of record becomes possible by reading with the light of smaller energy than the threshold energy.

14. Photochromic liquid crystalline systems

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Kinetic studies on photochromic molecules dissolved in thermotropic as well as lyotropic mesophases have been carried out to elucidate effect of microenvironmental structures of liquid crystal phases on photochromic reactions, in particular on thermal reversion processes which are retarded in general in smectic phases whereas there is no marked difference between nematic and isotropic phases. A combination of photochromism and liquid crystal phases brings about novel photo-optical effects to lead to photochemical ways to regulate optical properties of liquid crystals. The photochromic liquid crystal systems are classified into two groups whether photochromic molecules are incorporated in mesophases or bound onto substrate surfaces. One of the representative examples of the first involves photoinduced reversible mesophase alteration between nematic and isotropic phases. When a layer of a liquid crystal polymer substituted with azobenzene is illuminated with linearly polarized light, uniaxial reorientation of the chromophores takes place to induce optical anisotropy. The second type of photoresponsibe liquid crystal systems is assembled by sandwiching a nematic liquid crystal between a couple of substrate plates which are covered with photochromic molecular layers. Irradiation for surface photochromism leads to reversible alteration of liquid crystal alignment between homeotropic and planar modes. Furthermore, surface-assisted in-plane reorientation of mesophases is achieved by exposure to linearly polarized light to give rise to homogeneous alignment. These photoresponsive liquid crystal systems are of practical significances to applying to various optical devices.

15. Photochromic LB multilayers and its application to optical computer devices

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The Langmuir-Blodgett (LB) film is a mono- or multi-layered molecular assembly which is prepared by transferring a compressed monolayer spread on a water surface onto a solid substrate. With the LB multilayer film, one can obtain a molecular stacking architectures in which different kinds of dyes as donor and acceptor molecules are stacked sequentially such that the excitation energy transports layer-to-layer through the Förster dipole-dipole interaction mechanism. The fluorescences are emitted successively from respective layers associated with the excitation transfer from the outer surface to the inner layer. One can examine the kinetic behavior of this sequential excitation transport by measuring the ps time-resolved fluorescence spectrum. When a photochromic LB monolayer containing spiropyran, as an example, is incorporated in the LB multilayers, the transport of excitation can be switched depending on the reversible photochromic reaction between spiropyran and merocyanine upon irradiating with UV or visible light. We can monitor the switching of energy transport by measuring the fluorescence intensities of particular layers. This type of photochromic LB film may function as a two-dimensional (2D) and optical switching molecular device. The logics between the input signals (P_1 and P_2) and the output can be taken as AND, OR, NAND, NOR, P_1, $\overline{P}_1$, $\overline{P}_1 P_2$, $P_1 \overline{P}_2$, $\overline{P}_1 + P_2$ and $P_1 + \overline{P}_2$. All these correlation schemes are performed through selection of the wavelength(s) of the irradiation light as input and of the fluorescence emission(s) as output.
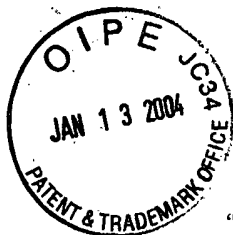
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(Page 184, paragraph 3. 2. to page 185, line 9)

3. 2   Structural change due to light

3. 2. 1 Photochromism

   a.   Definition

   Photochromism is defined as reversible change (A$\rightleftharpoons$B) of a single compound which is caused due to a photoelectromagnetic wave in at least one process between two states having different absorption spectrum to each other.   Hereinafter, the process in which thermodynamically stable A is converted to B due to photoexcitation is referred to as "positive reaction" and its reverse process is referred to as "reverse reaction". Further, when photochromsim is developed for various functional substances and materials, it becomes important whether the reverse reaction occurs due to only light or also due to heat. There is a suggestion that the former is called as P-(photochemical) type and the latter is called as T-(thermal) type. Most of photochromic compounds which have been ever known belong to T-type. However, thermal reverse reaction has a wide range of from a very fast progression in which its observation is difficult in room temperature, to a very slow progression. On the other hand, photochemical progression of the reverse reaction is difficult. Colored compounds which progress due to heat do not fade by irradiation of a visible light. Therefore, it is useful to apply them to a light quantity –adjusting material. This photochromism is sometimes called particularly as heliochromism.

(Page 189, paragraphc to Page 190, line 3)

C. Photochromic characteristics

1

There is a test method according to JIS to evaluate color fastness of a photochromic compound, wherein a test specimen is exposed to a light using direct rays of the sun or a weatherability tester and each degree of color change and color disappearance is judged by gray scale for color change and color disappearance immediately after exposure of a light and after standing for a prescribed time in a dark place.

From its practical viewpoint, a method comprising performing continuously irradiation with a weatherability tester and determining half value period in the degree of coloration due to a light has been often applied.

(Page 191, lines 5 to 6)

Each sensitivity of color development and color disappearance depends on quantaum yield (ϕ) $\times$ absorption coefficient (ε).

日本化学会 編

第4版 実験化学講座 12

物質の機能性

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3・2 光による構造変化

3・2・1 フォトクロミズム

a. 定　　義

フォトクロミズム (photochromism) は, 単一の化合物が異なる吸収スペクトルをもつ二つの状態間を少なくとも一つの過程が光電磁波によって引き起される可逆的な変化 (A ⇄ B) と定義される[1]. ここで, 熱力学的に安定な A が B へ光励起により変

換される過程を順反応，その逆の過程を逆反応ということにする．さらに，フォトク
ロミズムを種々の機能物質，材料に展開する場合，逆反応が光でのみ起るか，あるい
は熱によっても起るかが重要となるので，前者を P-(photochemical) 型，後者を T-
(thermal) 型と呼ぶ提案もある[2]．これまでに知られているフォトクロミック化合物
の多くは T-型に属する．ただし，熱的な逆反応は室温では観測困難なほど早い場合
から極めてゆっくり起るものまで幅広い．一方，逆反応が光化学的に起りにくく，熱
によって進行する化合物は着色体が可視光照射によっても退色しないので，サングラ
スのような光量調節材に有用であり，このフォトクロミズムを特別にヘリオクロミズ
ム (heliochromism) と呼ぶ場合もある[3]．

　三つ以上の状態を光により可逆的に変化する多値フォトクロミズムともいうべき現
象が知られている．化合物 (1) は紫外線照射により吸収スペクトルの異なる2種類の
閉環化合物となり，ポリフォトクロミズム (polyphotochromism) を示す[4]．4値フォ
トクロミズムは2種類のスピロジヒドロインドリジンが共役した化合物 (2) で実現さ
れている[5]．
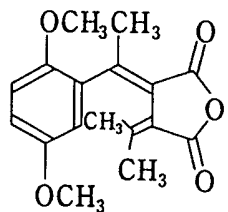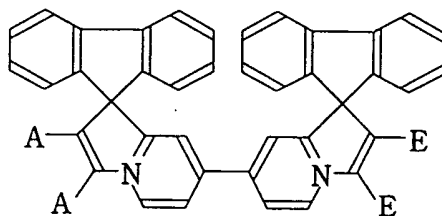
(1)　　　　　　　(2) (A = COCH₃, E = COOC₂H₅)

　上記定義における二つの状態 A と B は，分子構造の異なる化学種に相当する．同
一分子が分子分散状態と集合状態を可逆的に変化してもフォトクロミズムとなり得
る．3値フォトクロミズムの例であるが，2値フォトクロミズムの代表例であるニト
ロスピロピランを Langmuir-Blodgett 膜として光照射すると，分子分散状のメロシ
アニン構造を経てそれとは吸収が異なる J-会合体に落ち着く．これは熱もしくは光
によってスピロピランに戻る[6]．

　1960年代までのフォトクロミズム研究に関しては Brown 編の成書[1]があるが，そ
れ以降の進展が成書としてまとめられ[7]，その全容を把握するうえで有益である．本
項のフォトクロミック化合物についての記述はこの成書を参照にしている．その他に
多くの総説が発表されている[8]．

b. フォトクロミック化合物

電子環化反応に基づくフォトクロミズムとして，$4\pi, 6\pi, 10\pi$ 電子系がこれまでに知られている．

4π 電子系環化反応として，1,3-ジエンのシクロブテンへの光閉環反応は数多く知られているが，フォトクロミズムとしては見るべきものはない．しかしながら，シグロプロピルアニオンの等電子系であり，一つ以上のヘテロ原子を含む複素三員環，すなわち，オキシラン[9]，アジリジン[10]，ジアジリジン[11]，オキサジリジン[12] が関与するフォトクロミック化合物がある．それぞれ大きな極性変化を伴う特徴を有する．

6π 電子系環化反応によるフォトクロミック化合物は多い．その中で，数多くのスピロピラン誘導体が成書[1,7]にまとめられている．スピロピランの一般式は (3) で表現されるが，ピラン環に対する複素環の種類によって 20 種に及ぶ基本骨格が知られている．これらスピロピランがすべてフォトクロミズムを示すのではなく，基本骨格の種類とともに，置換基の効果を顕著に受ける．最も光着色に優れた誘導体の一つがニトロ置換体 (4) であるが，光劣化が起りやすい難点がある．(4) の酸素原子を硫黄原子に置換したチオスピロピラン誘導体は，その光着色体であるメロシアニン構造の吸収帯は著しく長波長にシフトする．

スピロピランの類縁体として合成されたスピロオキサジン（例えば (5)）は，紫外線照射に優れた耐久性を有することが見出され[13]，有機フォトクロミック材料として実用に供されるに至った．

(3)   (4)   (5)
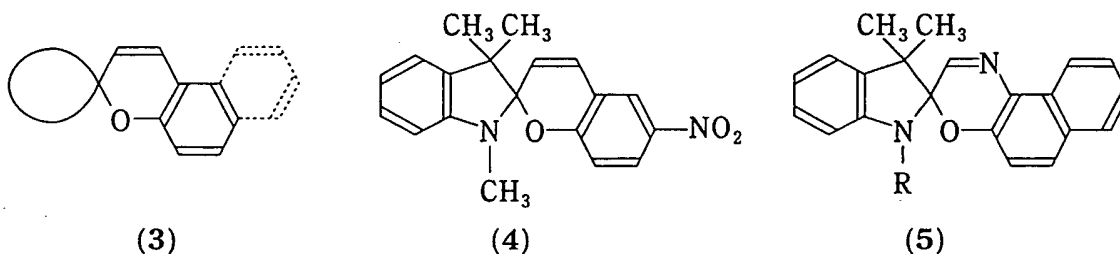
複素環フルギド (6)，もしくはその光閉環体 (7) の R^3 をメチルなどで置換することによって，可逆性と光着色体の熱安定性が著しく向上する[14]．フラン，チオフェン，ピロールのほかに，インドール，オキサゾール，チアゾール，ピラゾールなど多種類の複素環フルギドが合成されている[15]．R^1 が水素では (6) の E-Z 光異性化が主反応となるので，(7) に閉環するには R^1 がアルキル基である必要がある．R^3 はメチル基，R^4 は水素，メチルまたはフェニル基が多い．Y は酸素，硫黄，窒素に置き換えるにつ

れて (7) の吸収極大波長は赤色シフトする．R^2 の立体効果は (7) から (6) に戻る量子収率に大きな影響を与える．(8) のような R^1, R^2 ともにかさ高い化合物のフォトクロミズムは良好な量子収率を示す．
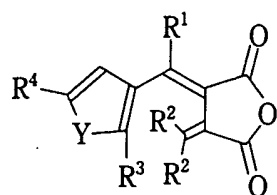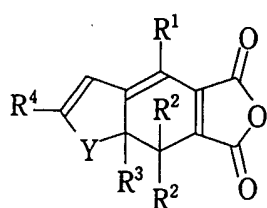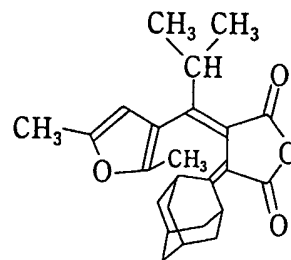
(6)   (7)   (8)

フルギド類はコハク酸ジエステルに 2 回アルドール縮合によるメチレン基導入により合成されるが，アセチレン化合物から一段でフルギド ((6) において Y＝O, S) を合成する反応が報告されている[16]．

cis-スチルベン[17] あるいはその誘導体 (9)[18] を紫外線照射すると $4a, 4b$-ジヒドロフェナントレンが可逆的に生成するが，$4a, 4b$ が水素置換体であれば不可逆反応が併発する．フルギドの場合と同様に，フェニル基を 2-位にメチルで置換された複素環に置き換えたジアリールエテン誘導体 (例えば，(10)，(11)) が合成され[19]，このような不可逆反応の防止と着色体の著しい安定化 (P-型化) が認められている．さらに，繰り返し安定性にも優れた化合物が見出されている[20]．
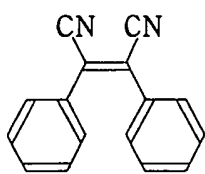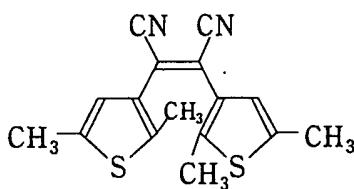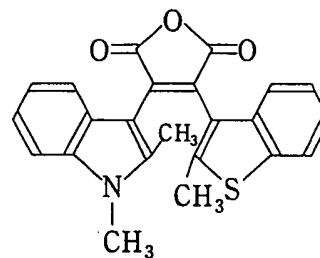
(9)   (10)   (11)

この種の 1, 3, 5-ヘキサトリエン構造に由来するフォトクロミズムは共役系にヘテロ原子が含まれていてもよい．一つの酸素原子を含むクロメン (12)[21] や二つのヘテロ原子を含むトリエン系である $2H$-1, 4-オキサジン (13)[22] は類似したフォトクロミズムを示すが，典型的な T-型である．

スピロ [1, 8a] ジヒドロインドリジン (14) の開環構造における荷電状態は，スピロピランやスピロオキサジンの場合と逆に，五員環炭素が負の電荷を帯びている．この

T-型フォトクロミズムは Dürr によって見出され，体系的に研究されている[23].

$$(12) \qquad (13) \qquad (14)$$
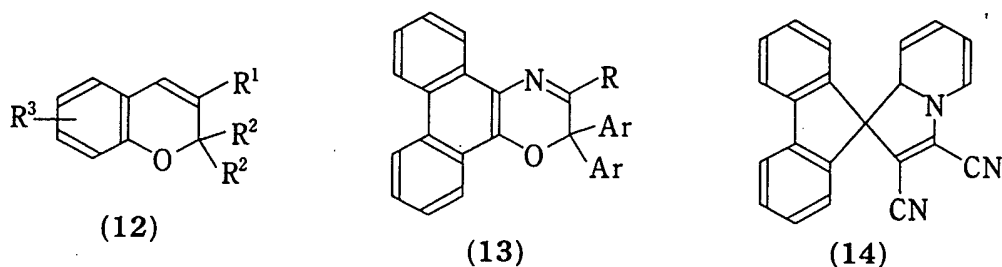
10π 系電子環化反応に基づくフォトクロミズム（(15)→(16)）が，一例報告されている[24].

$$(15) \qquad (16)$$
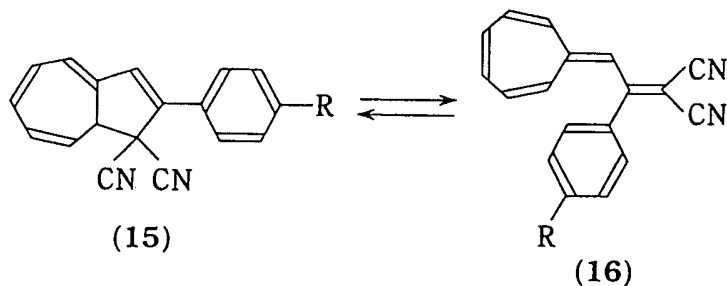
電子環化付加反応によるフォトクロミズムは分子内反応である．[2+2] 環化付加反応としてのノルボルナジエン-クアドリシクレン（(17), (18)）の相互変換は分子内環化付加反応であるが，感光波長の拡張のために三重項増感[25]や置換基導入[26]がなされている．これらの化合物は光エネルギーの化学的貯蔵を目的とする研究対象としても注目されている[27].

$$(17) \qquad\qquad (18)$$
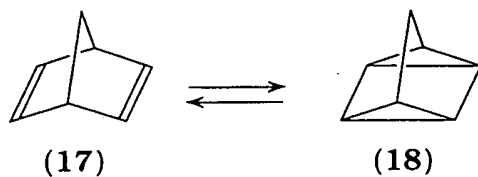
芳香環が共役したエチレン性化合物，例えば，ケイ皮酸誘導体，アセナフチレン，フェナントレンなど光照射によるシクロブタン形成は可逆的であり，フォトクロミックである．このフォトクロミズムは二分子反応に基づくので，二つのエチレン性化合物をアルキレン鎖で結合して効率を向上させる[28].

ナフタレン，アントラセンあるいはアクリジニウム塩に代表される芳香族化合物は可逆的な [4+4] 環化付加型二量化反応によるフォトクロミズムを示す．[2+2] 環化付加反応の場合と同様に，二つの発色団を一本鎖で結合したり，あるいは，二本鎖で結合してシクロファン型とすることによって，フォトクロミズムの高効率化が図ら

れる[29]．二分子のアントラセンは γ-シクロデキストリンに包接するので，2:1の錯体状態で効率よく可逆的な環化付加反応を起す[30]．

アントラセン骨格を内蔵する芳香族多環化合物（19）に酸素の存在下で可視光照射すると，一重項酸素が［4+2］付加したエンドペルオキシド（20）が生成し，共役が切れるために短波長へシフトする[31]．このような可逆的酸素付加脱離反応を示す多数の多環化合物が合成されている．
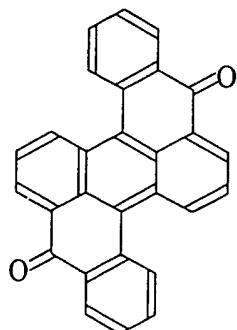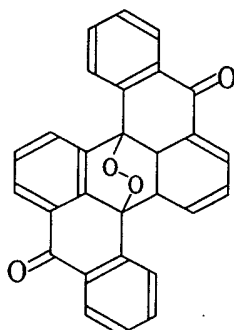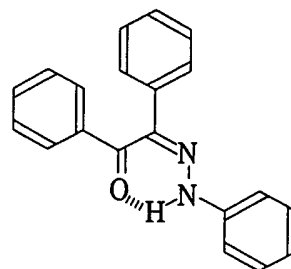
（19）　　　　　　（20）　　　　　　（21）

C＝C，N＝N 結合における光幾何異性化に基づくフォトクロミズムでは，吸収波長の変化量はあまり大きくない，C＝N 結合における光異性化においては，水素結合によって syn-体の安定性を高めることが有効である（例えば，（21））[32]．チオインジゴ類の異性体間での吸収極大波長の差は比較的大きいが[33]，合成が煩雑な場合が多い．

そのほかに，ビスイミダゾールの開裂反応[34]や水素移動に基づくサリチリデンアニリン（22），ニトロベンジル誘導体（23）など多様な化合物が知られている[35]．

一方，ビオローゲン[36]やキノン誘導体（24）[37]は光酸化還元反応に基づく可逆的な着色反応を示す．酸化の過程で酸素分子が消費されるので，厳密にはフォトクロミズムとはいえないが，顕著な光変色を起すことから関心がもたれている．
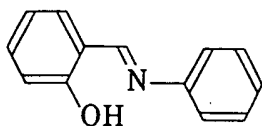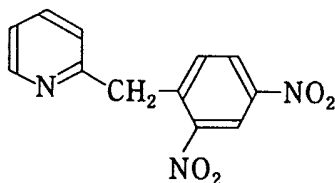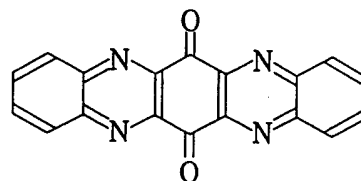
（22）　　　　　　　　　　（23）　　　　　　　　　　（24）

c.　フォトクロミック特性

フォトクロミック化合物を染色堅牢度として評価する JIS の試験法がある[38]．直射日光や耐光試験機を用いて試験片を露光し，露光直後および規定時間暗所に放置後に

おける変退色の程度を変退色用グレースケールによって判定する.

実用的な見地からは,耐光試験機で連続的に照射し,光着色の度合が半減する時間を求める方法が多くとられる.実験室的には超高圧水銀灯やキセノン灯によって連続的に照射し,光着色の程度を追跡する.ただし,これらは可逆回数の絶対評価ではなく,相対的な耐光性評価である[13].試験機内の温度が上昇するので T-型フォトクロミック化合物では着色体の形成量が少なく,この加速試験法による光劣化についての判定には注意を必要としよう.

超高圧水銀灯やキセノン灯からの集光した光路に 2 種類の色ガラスフィルターを交互にセットし,2 種類の波長の光を取り出して試料に照射する.筆者らは 500 W 超高圧水銀灯を光源とし,フィルター交換を所定の時間で自動的に行う照射装置を試作した.光着色と光退色がそれぞれ定常状態に達する条件で,1 サイクルを 5 秒程度で繰り返す.

繰返し特性に特に優れた材料評価や耐光性と分子構造との相関を調べるためには,さらに迅速な評価装置が必要となる.Gautron らは多数のスピロピラン誘導体の光劣化を評価しているが[39],光源としてキセノンフラッシュランプを用いている.光着色の吸光度が半減するサイクル数を耐光性の指標としている.入江はいくつかの代表的なフォトクロミック化合物の繰返し特性評価に,XeCl エキシマーレーザーとキセノンフラッシュを組合せた交互照射系を採用した[40].鈴木らは XeCl エキシマーレーザーとそれによって発振する色素レーザーを図 3・34 のように構成し,光路に挿入したミラーの開閉によって交互に試料に紫外線と可視光を照射する装置を用いている[41].これによって,アゾベンゼン誘導体の光劣化に対する置換基効果を認めている.任意の 2 種類の波長で高速に交互照射するには,2 台の色素レーザーを組み合せればよい.これまでの有機系フォトクロミズムの可逆回数はたかだか 10^5 程度であるが,これ以上に高い可逆性,例えば,10^6 サイクルを 1 時間で評価するためには,1 サイクルに要する時間は 36 μs となる.このような短時間照射は高輝度露光を意味し,発熱の除去が重要となる.

スピロオキサジンは良好な耐光性ゆえにすでに実用に供せられているが,繰返し特性(回数)に優れた化合物として,サリチリデンアニリン(5×10^4)[42],ジアリールエテン($>1.1\times10^4$)[20],ヘミチオインジゴ(10^5)[43]がある.

フォトクロミズムの光劣化機構の研究は十分とはいえない.アゾベンゼンは水素引

抜きによる還元反応あるいは誘導体によっては酸素酸化反応によって劣化する[44]．酸素酸化による分解はスピロインドリジン[45]や芳香族多環化合物[46]などでも認められる．一方，スピロピランの劣化がその三重項状態から起るので，分子内に三重項消光剤を結合すれば可逆性が向上する[47]．

フォトクロミック化合物の着色あるいは退色感度は量子収率（ϕ）×吸光係数（ε）に依存する．ϕ を向上させる一般的な指針はまだないが，前述のフリルフルギドに関しては立体効果が重要な要素となっている．連鎖的なフォトクロミック反応はまだ知られていない．cis-スチルバゾリウム塩のルテニウム錯体増感によるトランス体への光異性化[48]やクアドリシクレンからノルボルナジエンへの原子価異性化[49]といったdown-hill な逆反応過程が連鎖的に起り $\phi > 1$ となるが，順反応はこれらの触媒の存在下では起らないので，このままでは連鎖的なフォトクロミズムにはならない．

フォトクロミック分子の構造変化がそれを取り囲む媒体分子の状態を可逆的に変化させることができれば，その変化を光学的に検知する増幅系が原理的に可能となる．最も精巧なメカニズムを視覚に見ることができる．媒体が液晶などの非線形な状態変化を示すならば，線形なフォトクロミック反応を非線形系に変換できるので，見掛けの高感度化は可能である[33]．

T-型フォトクロミック化合物の逆反応速度を制御できれば，実用上好ましい．媒体の状態変化を利用する試みがなされており，以下に数例あげる．高分子マトリックス中での熱的な逆反応速度は，フォトメロシアニンの例にあるように，ガラス転移温度で不連続に変る[50]．液晶相中にフォトクロミック化合物を溶解すると，熱的な逆反応速度が低下する[51]．二分子膜の結晶-液晶相転移も逆反応速度に大きな影響を与える[52]．長鎖アルキル基をもつスピロピランのLB膜に紫外線を照射すると，フォトメ

MS：ミラーシャッター，D：ディテクター，
M：ミラー

図3・34 フォトクロミック化合物の繰返し
　　　　耐光性評価
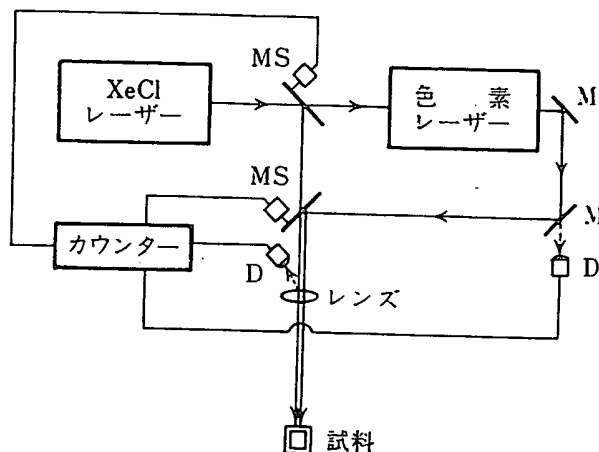
ロシアニンは安定な J-会合体となり，通常のフォトメロシアニンに比べて約 10^4 倍安定化する[6]．スピロピラン[53]やスピロオキサジン[54]を金属イオン存在下で光照射してフォトメロシアニンなどのキレートととし，着色体を安定化する方法もある．

d. フォトクロミック材料

フォトクロミック分子とそれを取り囲む媒体との相互作用が特異的であれば，フォトクロミズムに基づく分子構造変化を吸収スペクトル変化にとどまらないさまざまな材料物性変化に変換することができる．表3・12 に誘起される例をまとめる．これらは分子集合系のフォトクロミズム[8d]によって引き起される物性変化であり[55]，光応答性のさまざまな機能発現に直結する．光機能との関連で興味をもたれている系はフォトクロミック液晶であり，その研究例のみを以下に記す．

液晶がもつ複屈折性をフォトクロミック反応によって制御することができる．液晶にフォトクロミック分子を溶解すれば，その光反応に応じた分子構造変化がネマティック相[56]やコレステリック相[57]の相変化を引き起す．それ自体メソゲンとなりうるアゾベンゼンや著しい分子構造変化を示すスピロピラン (4) がよく用いられる．高分子液晶においても光誘起相転移が起るが，そのガラス状態では分子運動が束縛されるために相転移状態が凍結される特徴を示す[58]．直線偏光で n-π^* 励起によるアゾベンゼンの光異性化を高分子液晶中で行うと，アゾベンゼン分子長軸が再配列して偏光軸と直交し，それに伴ってメソゲンの再配向が起る[59]．アルゴンレーザーからの 488 nmの光により，回折効率（>50%）の高い書換え可能なホログラム記録が可能となる．

ネマティック液晶分子の配向は，基板表面に結合した単分子状のアゾベンゼンの光異性化によって制御される[60]．すなわち，トランス体ではホメオトロピック（垂直）

表 3・12 フォトクロミズム（PC）に伴う材料物性変化

特　性	構　　造　　変　　化	
	PC分子構造レベル	マトリックス構造レベル
光学的	吸収スペクトル，発光スペクトル 屈折率	吸収スペクトル，発光スペクトル 屈折率 光散乱，複屈折，旋光性，反射率
化学的	キレート形成，イオン解離 エンタルピー	キレート形成，イオン解離 エンタルピー 触媒作用，酵素活性，膜透過
電気的 バルク	相変化，溶解性	誘電性，光導電性，膜電位 相変化，溶解性 粘度，濡れ性，密度，弾性

配向であるが，シス体ではパラレル（平行）配向となる

3・2・2　フォトケミカルホールバーニングとフォトンエコー

a.　測定原理

（i）　均一幅と不均一幅　　多くの物質の光吸収や発光スペクトルは，ある周波数範囲に広がった強度分布をもっており，通常そのスペクトル幅は均一幅と不均一幅により説明される．同種の複数の分子が均一な場（無秩序に変動する場を含む）におかれた場合，観測されるスペクトル幅は，均一幅となる．均一幅は Heisenberg の不確定性原理によれば光励起状態の寿命の逆数となる．一般に，光励起状態の寿命は二つの時間パラメーター，すなわち位相緩和時間（T_2）とエネルギー緩和時間（T_1）を用いて記述される．位相緩和時間とは，コヒーレントに励起された状態が，外場の影響によりその振動の位相に乱れを生じる時間であり，エネルギー緩和時間とはその振動のエネルギーが失われていく時間である．T_1, T_2 時間を用いて均一幅 Γ_h(Hz) を式 (3・74) のように表すことができる．

$$\Gamma_h = (1/2T_1 + 1/T_2)/\pi \tag{3・74}$$

一方，個々の分子スペクトルに影響を与える物理量が統計的分布をもつ場合には，均一幅よりも広がったスペクトル幅が観測される．これが不均一幅である．気体において観測される Doppler 広がりは不均一広がりの一例である．固体でも多くの物質系で不均一広がりが観測される．例えば，透明なポリマー中にドーピングされた色素の光吸収スペクトルは，低温において均一幅よりかなり広い不均一幅をもつことが多い．この場合，互いに相互作用しない色素は局在電子系と考えることができ，その光吸収スペクトルは個々の電子系のスペクトルの統計和となる．個々の電子系のスペクトルは，それらと相互作用するポリマーマトリックスの局所場に強く影響される．局
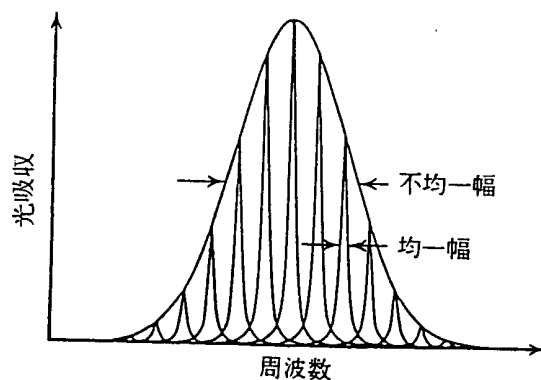
図 3・35　均一幅と不均一幅

置やプロトン移動のしやすさを制御することが可能である.

　上では, 分子内でのプロトン移動の制御について述べたが, 結晶中で分子間のプロトン移動を制御し新しい機能を発現させようという試みも最近活発に行われている. キノンとヒドロキノンからなるキンヒドロンは, 最も古くから知られた電荷移動錯体の一つである. この結晶では, 分子の積層方向に軌道の重なりによる電荷移動相互作用があり, 分子積層間に水素結合が存在する (図3・70左上). この結晶に圧力を加えていくと, ヒドロキノンからベンゾキノンへ電子とプロトンが移動することによってセミキノン状態 (図3・70右下) が実現することが赤外および可視吸収スペクトルの測定から示唆されている[107,111]. この相転移は, 積層方向の電荷移動と積層間のプロトン移動が協力して起る新しいタイプの相転移とみることができ, 相転移点近傍での光学応答, 電場応答や磁気的性質の変化に興味がもたれている. このほか, 分子の末端に―C=O 基と=C―OH 基をもつオキソカーボン系分子からなる水素結合結晶において, 分子間プロトン移動とそれに伴う常誘電性, (反) 強誘電性の発現に関する研究も行われている.

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[Photochromism]

It means the phenomena that a substance species changes its color in the state of a solid or a solution by irradiation of a light (an ultraviolet light or visible rays) and again reverts to its original color in a dark place (generally the reverting speed is low). It is also called as photochromy or phototropy. The cause of color change includes photoisomerization due to transfer of a hydrogen atom, production of free radical due to dissociation and opening of ring. However, its mechanism is not sufficiently established. Examples of the substance exhibiting photochromism includes inorganic compounds such as $Hg_3S_2I_2$ and ZnS, and organic compounds such as hydrazine, oxazone, stilbene, derivatives of salicylaldehyde. spiropyrane or biimidazolyl and bianthrone. Most of these organic compounds remarkably changes from colorlessness or light yellow to blue, violet or red violet. It is known that the substance exhibiting photochromism exhibits thermochromism (reversible color change to be generated due to heat similar to photochromism) or piezochromism (reversible color change to be generated due to intense grinding of a solid or under an applied pressure).

岩波 理化学辞典

第4版

久保亮五　長倉三郎
井口洋夫　江沢洋
編集

フォト [photo] =光下.

フォトカプラー [photo coupler]

フォトクロミズム [英 photochromism, 独 Photochromie, 仏 photochromie, 露 фотохромизм]

フォトダイオード [photodiode]

フォトトランジスター [phototransistor]

フォトレジスト [photo-resist]

フォートラン [英 仏 独 FORTRAN 露 ФOPT. PAH] formula translation（数式翻訳）に由来し、計算機のプログラム言語の一つ。1957年頃IBM社のバッカス(J. Backus)らが開発した。

フォトエコー [英 photoecho 独 фotoecho]

フォルステライト [forsterite] ケイ酸二マグネ

フォルタン気圧計 [Fortin barometer] →気圧計.

フォルハルト法 [Volhard method] [1] 銀滴定

フォルマント [formant]

フォン [英 phon 独 Phon]

フォノン [英 仏 phonon 独 Phonon 露 фonon]

フォノンドラッグ [phonon drag]

フォノンメーザー [phonon maser]

フォーブッシュ減少 [Forbush decrease]

フォールアウト [英 fallout 仏 retombée 独 Ausfall 露 радиоактивное выпадение] 核爆発実験など

フォン・オイラー [von Euler, Ulf Svante] 1905. 5.10. スウェーデンの生理学者。1929年度発疹チフスを受賞し、... (von Euler-Chelpin, Hans Karl August Simon, 1873.2.15-1964.11.6.) の息子。ストックホルム医科大学、1939年カロリンスカ研究所の生理学教授、1946年スウェーデン王立学士院会員。1939年以来、神経学賞審査委員長をつとめ、1953-65年度ノーベル生理学医学賞選考委員会であった。1970年度ノーベル生理学医学賞を受けた。

フォン・ノイマン [von Neumann's condition] 線形偏微分方程式の初期値問題を近似する差分方程式の安定性の条件を与えみ...

フォン・ノイマンの一意性定理 [von Neumann's uniqueness theorem] →正準交換関係の表現.

フォン・ノイマンの条件 [von Neumann's condition]

負荷 [英 load 仏 charge 独 Last, Belastung 露 нагрузка]

付加化合物 [addition compound]

不可逆過程 [英 irreversible process] →不可逆変化.

不可逆反応 [英 irreversible reaction 仏 réaction irréversible 独 unumkehrbare Reaktion, irreversible Reaktion, 露 необратимая реакция]

不可逆過程の熱力学 [仏 thermodynamique irréversible 独 thermodynamik irreversibler Prozesse 露 термодинамика необратимых процессов] →非平衡熱力学.

不可逆素子 [non-reciprocal (circuit) element] →ジャイレーター.

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KIRK-OTHMER

ENCYCLOPEDIA OF CHEMICAL TECHNOLOGY

THIRD EDITION

VOLUME 18

PLANT-GROWTH SUBSTANCES
TO
POTASSIUM COMPOUNDS

POLYCARBONATES

Polycarbonates (PC) are a special class of polyesters derived from the reaction of carbonic acid derivatives with aromatic, aliphatic, or mixed diols. They may be produced by the Schotten-Baumann reaction of phosgene with a diol in the presence of an appropriate hydrogen chloride acceptor (eq. 1) or by a melt transesterification reaction between the diol and a carbonate ester (eq. 2) (see Esters).

$$n \; HOROH \; + \; n \; COCl_2 \; + \; (2n + 1) \; NaOH \; \longrightarrow$$

$$Na \!-\!\!\underset{}{\overset{O}{\underset{\|}{(OCOR)}}}\!\!\overline{}_n\!-OH \; + \; 2n \; NaCl \; + \; 2n \; H_2O \qquad (1)$$

$$n \; HOROH \; + \; n(R'O)_2CO \; \xrightarrow{\text{catalyst}} \; R' \!-\!\!\underset{}{\overset{O}{\underset{\|}{(OCOR)}}}\!\!\overline{}_n\!-OH \; + \; (2n - 1) \; R'OH\!\uparrow \qquad (2)$$
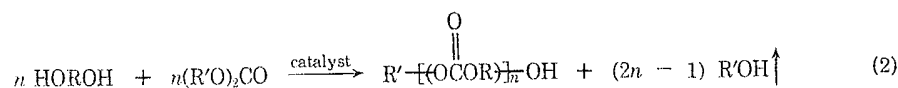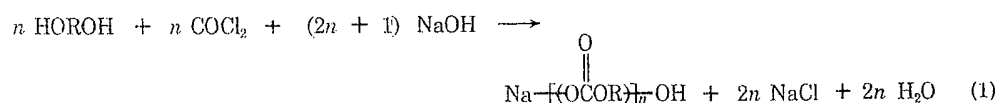
The three dihydroxybenzenes, hydroquinone, resorcinol, and catechol react with phosgene in pyridine (1). Hydroquinone and resorcinol yield polymers, whereas catechol produces a cyclic carbonate. The hydroquinone polymer is crystalline, insoluble, and infusible. The resorcinol polycarbonate is an amorphous (glassy) material melting about 200°C. These polymers are no doubt of low molecular weight, especially the hydroquinone polycarbonate. Later, similar polymers were synthesized via a transesterification reaction between hydroquinone or resorcinol and diphenyl carbonate (2). In the late 1920s and early 1930s, aliphatic polycarbonates were included in the systematic exploration of polyesters but the low melting polycarbonates did not yield products of commercial interest (3).

In 1941, Pittsburgh Plate Glass Company (PPG) introduced its liquid casting resin designated CR-39 (4). This material is reported to be the product of the reaction of diethylene glycol chloroformate with allyl alcohol. It may be polymerized (peroxide initiated) to yield a highly cross-linked, colorless, scratch-resistant, transparent unsaturated dicarbonate plastic which is used in optical applications. Although technically outside the scope of this review, plastic objects derived from CR-39 are described as polycarbonates. This product, which is still on the market, could thus qualify as the first commercial polycarbonate. Akzo Chemie has just started up a new plant in the United Kingdom for its manufacture (5) (see Allyl monomers and polymers).

Aromatic polycarbonates were rediscovered approximately fifty years after the early hydroquinone and resorcinol experiments. The polycarbonate of bisphenol A (2,2-bis(4-hydroxyphenyl)propane) was synthesized independently both at Bayer A.G. and General Electric. Because of its unusual and attractive characteristics, each company initiated a development program. Bayer A.G. first announced a series of polycarbonates derived from assorted biphenols (6). The basic General Electric patent (7) claims the transesterification process and its products, whereas the Bayer patent (8) claims an interfacial polymerization process and has multiple claims to aromatic polycarbonates. Interest in aromatic polycarbonates spread rapidly and many different companies entered the field to try to establish proprietary niches based on this new, high heat-stable, mechanically tough, transparent, engineering thermoplastic. More than 100 aromatic polycarbonate patents have issued to more than 30 different companies in the interim (see Engineering plastics).

BISPHENOL A POLYCARBONATE

Properties and Characterization

Solvents, Solubility, and Solvent Resistance. Most of the commercial polymer is produced and characterized in solution. Some is converted to film, whereas solutions are used to apply coatings to polycarbonate parts. The solvents may crystallize, craze, crack, or mar the surface of objects made from polycarbonates. Chloroform, *cis*-1,2-dichloroethylene, *sym*-tetrachloroethane, and methylene chloride are the preferred solvents and the last is the material of choice (9–10). Methylene chloride is an excellent solvent (350 g polymer/L solvent at 25°C) with the advantages of low flammability and toxicity. Pyridine, cresylic acid solvents, and *p*-dioxane (60 g polymer/L solvent at 25°C) are the nonhalogenated solvents. Hydrocarbons and aliphatic alcohols, esters, and ketones do not dissolve polycarbonates. Chlorobenzene, which may be used in the processing of polycarbonates, is an adequate high temperature solvent, but the polymer may crystallize and set to a hard gel state on cooling. Acetone promotes rapid crystallization of the normally amorphous polymer, and causes catastrophic failure of stressed polycarbonate parts. Aliphatic and aromatic hydrocarbons promote crazing of stressed molded samples. Care must be exercised in the choice of solvents for painting and coating operations.

Bisphenol A polycarbonate [25037-45-0] exhibits high hydrolytic stability. Water has no effect at neutral or acidic pH, whereas dilute alkali slowly attacks the surface. Boiling a polycarbonate film in dilute alkali etches the surface and the polymer slowly degrades and dissolves. The undissolved portion of the film retains its tensile strength. In another series of tests, polycarbonate film samples were subjected to steam at 101 kPa (1 atm) at 100 and 150°C to determine time to embrittlement (10). The samples failed after 700 and >200 hours, respectively. The hydrolytic stability can at least partly be attributed to the polymer's low water solubility and high glass-transition temperature. Solvents such as *p*-dioxane reduce resistance to hydrolysis.

Molecular Weight. Injection-molding grades of bisphenol A polycarbonate normally have intrinsic viscosities in the range of 0.50–0.55 dL/g, as determined in chloroform at 30°C. Extrusion grades may run slightly higher. Based on light scattering and osmometry data, a typical polymer with an intrinsic viscosity of 0.50–0.55 dL/g might have a weight-average molecular weight ($\overline{M}_w$) of 30,000 and a number-average $\overline{M}_n$ of 11,000 to yield a dispersity ratio $\overline{M}_w/\overline{M}_n$ of 2.7.

In a plot of positive trends in mechanical properties versus intrinsic viscosity, the slope is very steep until the intrinsic viscosity reaches 0.45 and then tapers off; that is, the values for all properties (tensile, impact, flexural strength, elongation, etc) are approaching maxima at intrinsic viscosity greater than 0.45 with a single very important exception. The melt viscosity continues to increase and can quickly render the material unprocessable. For example, polycarbonates with viscosity values above 0.6 are extremely difficult to inject into complex molds. Thus, a compromise is necessary between a polymer with sufficiently high viscosity to have maximum mechanical properties and a polymer with sufficiently low viscosity to have flow characteristics needed to fill intricate molds.

Crystallinity and Structure. The mechanical–optical properties of polycarbonates are those common to amorphous polymers. There may be some order, but it is insufficiently developed to result in loss of transparency or to be observed in routine x-ray spectra. The polymer, however, may be crystallized to some degree by prolonged heating at elevated temperature (8 d at 180°C) (11), or rapidly by immersion in acetone. Powdered amorphous polymer appears to dissolve partially in acetone, initially becoming sticky. It then hardens and becomes much less soluble as it crystallizes. This change may be confirmed by before-and-after x-ray diagrams that change from diffuse to sharp patterns.

Film or fibers derived from low molecular weight polymer (viscosity <0.5 dL/g) tend to crystallize and embrittle on immersion in acetone; those based on higher molecular weight polymer (viscosity >0.6 dL/g) become opaque, dilated, and elastomeric. When a dilated sample is stretched and dried, it retains orientation and is crystalline. An oriented crystallized film exhibits enhanced tensile strength. It is considerably higher at room temperature than that of amorphous film stretched to the same extent. In addition, the tensile heat-distortion temperature of crystalline film is approximately 20°C higher. The gas permeability is decreased and resistance to solvent attack is increased. Plasticizer-nucleating agents have been patented that assist crystallization of polycarbonates (12).

Glass-Transition Temperature and Dependent Properties. Bisphenol A polycarbonate has a bulky structure, and packing at the pivotal linkages tends to restrict rotation. Furthermore, the repeat units along the chain are longer than those of most common polymers, which makes ordered arrangement difficult. These features play a key role in determining the physical properties.

The T_g at 149°C for bisphenol A polycarbonate is unusually high compared to that of polystyrene (100°C), poly(ethylene terephthalate) (69°C), nylon-6,6 (45°C), and polyethylene (−45°C). At the T_g, an important determinant of many physical–mechanical properties, there is a significant onset of molecular mobility (rotation). A high T_g indicates excellent dimensional stability and resistance to creep under load, both properties of bisphenol A polycarbonate. The T_g essentially sets the upper temperature limit for maintenance of mechanical and electrical properties. From a practical standpoint, however, polymers are seldom used at their T_g.

Melt Behavior. Bisphenol A polycarbonate becomes plastic at the reported melting range of 215–225°C and it may be shaped with sufficient pressure. The viscosity continues to decrease with increasing temperature and over its normal injection-molding range of 270–315°C, the melt viscosity drops from 1100 to 360 Pa·s (11,000 to 3600 P). For comparison purposes, the melt viscosity of poly(ethylene terephthalate) of similar molecular weight is five times lower over the same temperature range (13). Inasmuch as the melt viscosity of bisphenol A polycarbonate is essentially independent of shear rate, processing melt viscosity can only be reduced by increasing the processing temperature. Fortunately, the thermal stability of bisphenol A polycarbonate is adequate to permit this.

Thermal Stability. Bisphenol A polycarbonate exhibits outstanding thermal stability. The dry polymer may be held for hours in the molten state up to 320°C and for short times up to 330–350°C with minimal degradation (6). Decomposition begins at an appreciable rate above this temperature and rapid cracking and loss of volatile fragments only occurs above 450°C (14). The outstanding thermal stability coupled with a high degree of aromaticity combine to make bisphenol A polycarbonate resistant

to burning. Its oxygen index at 26 is a quantitative measure of the thermal-oxidative stability, indicating that under test conditions an atmosphere comprised of 26% oxygen and 74% nitrogen is necessary to maintain combustion. The inherent fire resistance of the polymer may be further enhanced by incorporation of special catalytic additives or halogen-containing comonomers (15) (see Flame retardants).

Light Transmission.   Polycarbonate resins exhibit water-white clarity with visible-light transmission of approximately 90%. Haze is minimal (1–2%), absorption in the uv range is essentially complete, and penetration is very slight. Exposure to outdoor weathering causes yellowing and dulling of the surface. The refractive index of 1.586 is predictably high because of the high aromatic content.

Polycarbonates are frequently employed as lightweight, break-resistant glass substitutes in light-transmission applications. For example, transparent canopies for high speed military aircraft withstand impact with fowl at Mach-II speeds. The high impact strength, combined with transparency and high flexural strength, make polycarbonate sheet a candidate for bullet-resistant glazing. Both monolithic and laminated constructions are capable of stopping projectiles. The kinetic energy of a bullet is converted to heat and melts a partial or complete passage through the plastic without shattering. The projectile-stopping ability of bisphenol A polycarbonate appears to be an inherent property, that is, the energy-absorbing capacity per unit of thickness can be determined and the thickness calculated that is needed to stop a projectile with mass M moving at velocity V. The kinetic energy of the bullet on impact is $E_i = \frac{1}{2} M V_i^2$ and on exit $E_e = \frac{1}{2} M V_e^2$. The energy absorbed by the sheet of plastic is $E_a = E_i - E_e$. Energy absorption of the plastic is essentially independent of projectile velocity, whereas the bullet-stopping ability of glass increases with increasing velocity. The kinetic energy in the case of glass is apparently utilized in producing glass powder at very high speeds and large shards at low speeds. Laminated polycarbonate sheet is frequently used as protection against hand guns; a combination of laminated glass plus laminated polycarbonate sheet effectively stops very high speed rifle fire.

Because polycarbonate sheets and film lack the abrasion resistance of glass, numerous transparent hard coats have been developed to protect the surface (16). Screening agents against uv are incorporated in the protective coatings, which also provide resistance to solvent attack (17) (see Uv stabilizers).

Mechanical Properties.   The unusual mechanical properties of bisphenol A polycarbonate are given in Table 1. Whereas its room-temperature modulus and tensile strength are in the same range as those of other amorphous thermoplastics at corresponding reduced temperatures, its impact strength and ductility are altogether exceptional. Below their T_g, most amorphous polymers are stiff, glasslike, and brittle in tension and bending. Polycarbonate is an exception. The stress–strain curve in uniaxial tension (Fig. 1) is typical of ductile materials, consisting of an initial Hookean region, followed by (shear-induced) yielding and plastic deformation to a total breaking elongation of 120%. The area under the stress–strain curve, a measure of energy absorption per unit volume, is approximately 65 J/m³ (1.7 × 10⁻³ Btu/ft³). This is 8.5 times the energy absorption of die-cast aluminum, and 60% that of carbon steel.

Impact strength (a measure of ductility at high strain rates) is customarily measured by notched Izod, tensile impact, and falling-dart impact. Perhaps the most widely quoted value is that for notched Izod, which measures, according to a predetermined procedure, the energy absorption under impact conditions, of a sample containing

Table 1. Bisphenol A Polycarbonate, Properties of Injection-Molding Compound

Properties	Values	ASTM Test method[a]
Physical		
density, g/cm^3	1.200	D 792
water absorption, m, 24 h	0.15	D 570
equilibrium water, %	0.35	
light transmittance, %	86–89	D 1003
haze, %	1–2	D 1003
refractive index	1.586	
Thermal		D 648
heat deflection, °C		
at 1820 kPa[b]	132	
at 455 kPa[b]	138	
specific heat, kJ/(kg·K)[c]	1.26	C 351
linear thermal expansion per °C	6.75×10^{-5}	D 696
thermal conductivity, W/(m·K)	0.195	C 177
brittle temperature, °C	<−129	D 746
continuous-use temp, °C	121	
flammability, mm[d]	<25	D 635
UL standard		
3.18 mm thick	94 V-2	UL 94
1.5 mm thick	94 V-2	UL 94
oxygen index, %	25	D 2863
Electrical		
dielectric strength, mV/m (380 V/min)	15	D 149
dielectric constant		D 150
at 60 Hz	3.17	
at 2.96 Hz	2.96	
power factor		D 150
at 60 Hz	0.0009	
at 1000 Hz	0.010	
volume resistivity, cm	8×10^{16}	D 257
Mechanical		D 638
tensile strength, MPa[e]		
yield	62.1	
ultimate	65.5	
elongation, %		D 638
yield	6–8	
break	110	
tensile modulus, MPa[e]	2380	D 638
flexural strength, MPa[e]	93.1	D 790
flexural modulus, MPa[e]	2340	D 790
compressive strength, MPa[e]	86.2	D 695
Izod impact, J/m[f]		D 256
notched	860	
unnotched	no failure	
tensile impact, kJ/m^2 [g]	475–630	D 1822

[a] Unless otherwise stated.
[b] To convert kPa to psi, multiply by 0.145.
[c] To convert J to cal, divide by 4.184.
[d] Extent of burning.
[e] To convert MPa to psi, multiply by 145.
[f] To convert J/m to ftlbf/in., divide by 53.38.
[g] To convert kJ/m^2 to ftlbf/in.^{2}, divide by 2.10.
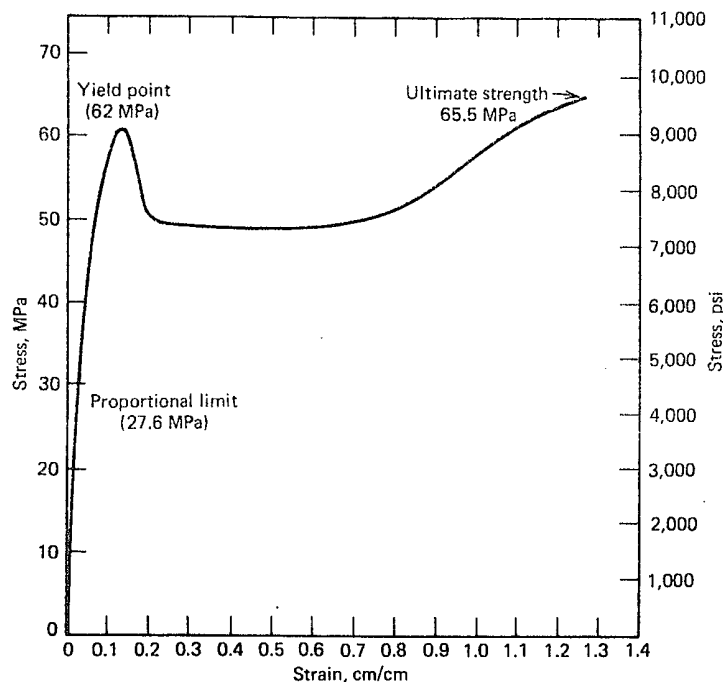
Figure 1.   Stress–strain curve for standard polycarbonate resins (23°). To convert MPa to psi, multiply by 145.

a notch or stress concentrator. Polycarbonates were rated as the highest impact-resistant engineering polymers until the equally impact-resistant supertough nylons were recently introduced (18). However, polycarbonates under high strain rate (impact) conditions are sensitive to the severity of stress concentrators present; in addition, this sensitivity is temperature- and thickness-dependent. At room temperature, increasing the severity of the stress concentrator (by decreasing the radius of the notch tip from 0.038 to 0.020 mm) reduces the notched impact strength from 960 to 130 J/m (18 to 2.4 ft·lbf/in.); moreover notched samples, when tested over a range of temperatures, show a similar transition from ductile to brittle notched-impact behavior at −10 to −20°C (Fig. 2). There is also an abrupt transition from ductile to brittle failure as the thickness of the notched-impact test bar is increased from 3.18 to 6.35 mm. This critical thickness phenomenon has been at least partially resolved by copolymerization of bis(4-hydroxyphenyl) sulfide with bisphenol A (19). The General Electric Co. has successfully resolved the critical-thickness issue (with loss of transparency) by means of a special formulation with impact modifiers in a high molecular weight grade of Lexan EM polycarbonates (Fig. 3).

The tensile-impact strength of PC remains high over an extended temperature range. Thus, the inherent high impact resistance of the material is maintained over a very broad temperature range, but the sensitivity to stress raisers must be taken into account in parts to be used in situations involving impact. Careful design is essential: for instance, avoidance of sharp corners.
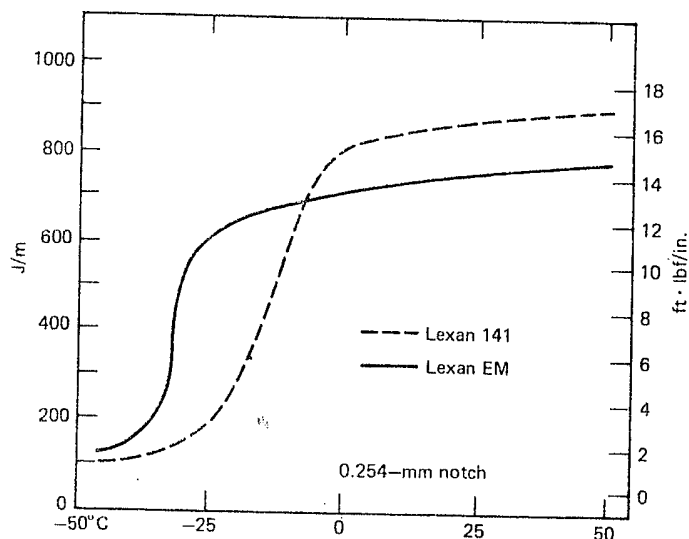
Figure 2.   Low temperature notched Izod impact strength.
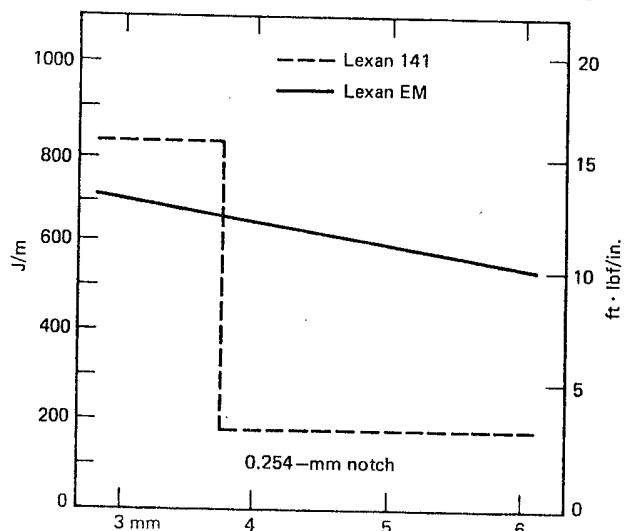
Figure 3.   Notched Izod impact-strength thickness effect.

Manufacture

Most commercial polycarbonates are derived from 2,2-bis(4-hydroxyphenyl)-propane. However, few details of commercial polymerization processes have been disclosed. Descriptions in the technical press and patent literature tend to be more conceptual than operational (63). At first, both direct-reaction and melt-transesterification processes were prepared. In the former, phosgene reacts directly with bisphenol A to form a polymer in a solution. In transesterification, phosgene first reacts with phenol to give a diphenyl carbonate, which in turn reacts with bisphenol A to give phenol and a molten, solvent-free polymer. Transesterification is reported to be the least expensive route. It was phased out, however, because of its unsuitability to

produce a wide range of products (21). The basic chemistry is shown in equation 3.
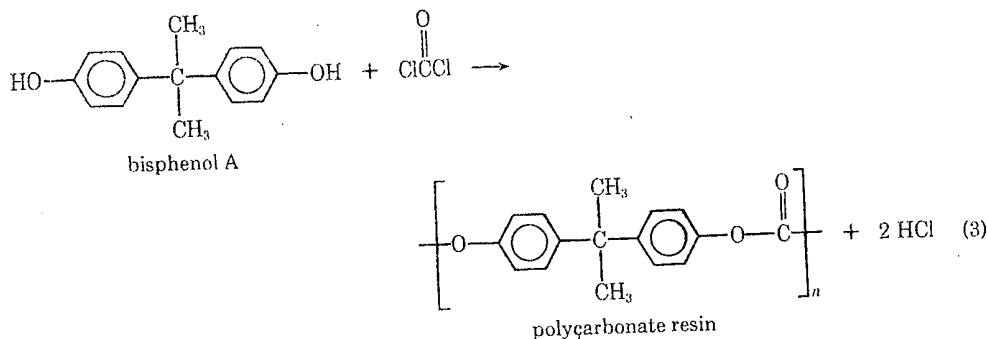
The reaction may be run in solution employing a polymer solvent such as methylene chloride and an acid acceptor such as pyridine (22). The polymer (mol wt 12,000–15,000) may be recovered as a methylene chloride solution after multiple aqueous washes to remove the pyridine hydrochloride formed and excess pyridine.

Most polycarbonate is produced by an interfacial adaptation of the reaction in equation 3 (23). The bisphenol plus 1–3 mol percent monofunctional phenol (which controls molecular weight) is dissolved or slurried in aqueous sodium hydroxide; methylene chloride is added as a polymer solvent, plus a catalytic quantity of a tertiary amine, and phosgene gas is dispersed in the rapidly stirred mixture. Additional caustic solution is added as needed to maintain basicity. The growing polymer dissolves in the methylene chloride and the phenolic content of the aqueous phase diminishes. By-product sodium chloride remains in the aqueous phase along with some carbonate salts obtained as by-product of the reaction of part of the phosgene with caustic. When the reaction is completed, ie, the phenols disappear from the aqueous phase, the phases are separated and the polymer solution is washed with water, extracted with acid to remove catalyst residues, and finally washed to neutrality with water.

Recovery processes for isolating the polymer from reaction solvents remain closely guarded trade secrets. Proposed procedures include nonsolvent precipitation, partial or complete solvent removal in boiling water followed by oven-drying, spray-drying, and multistep total solvent evaporation. The last includes wiped-film evaporators and finally stripping through multiport vacuum-vented extruders (24). The total removal of a low boiling chlorinated hydrocarbon from a very high viscosity, high melting polymer presents engineering challenges. When a methylene chloride solution of polymer is heated at relatively low temperatures, foam is produced which complicates heat and mass transfer and can lead to stalled equipment since the polymer has a high solidification temperature. Therefore, elevated pressure must be used initially to minimize foam formation while maintaining the polymer above its solidification point. This pressure can be reduced gradually and the temperature raised as the solvent removal is complete. The process is further complicated by the fact that methylene chloride, normally employed as polymerization solvent, reacts with and corrodes the machine. Wet methylene chloride forms pure acid on standing at low temperature, while dry methylene chloride yields HCl and corrodes at 60°C in contact with stainless steel. An intermediate solvent exchange is needed with a less corrosive solvent (generally chlorobenzene) before final solvent removal. In so-

lution extrusion, the polymer is recovered in the form of an extruded strand that can be cut to yield a naturally transparent, pelletized molding compound. However, many applications require pellets with widely differing formulations, eg, glass fibers, colors, stabilizers, and flame retardants, and a second extrusion operation is frequently needed. Isolation procedures that yield powdered polymers require rigorous drying to remove water and traces of solvent; all the powder must be extruded and pelletized, even in the case of naturally transparent formulations.

The basic transesterification reactions are shown in equations 4–5 (see also Alkylphenols; Phosgene).

$$2 \; \text{C}_6\text{H}_5\text{—OH} + \text{ClCCl} + 2\,\text{NaOH} \longrightarrow \text{C}_6\text{H}_5\text{—O—C(=O)—O—C}_6\text{H}_5 + 2\,\text{NaCl} + 2\,\text{H}_2\text{O} \quad (4)$$

$$n \; \text{HO—C}_6\text{H}_4\text{—C(CH}_3)_2\text{—C}_6\text{H}_4\text{—OH} + n \; \text{C}_6\text{H}_5\text{—O—C(=O)—O—C}_6\text{H}_5 \xrightarrow[\text{catalyst}]{\Delta}$$

$$\text{H}\Big[\text{O—C}_6\text{H}_4\text{—C(CH}_3)_2\text{—C}_6\text{H}_4\text{—O—C(=O)}\Big]_n \text{O—C}_6\text{H}_5 + (2n-1)\; \text{C}_6\text{H}_5\text{—OH} \quad (5)$$
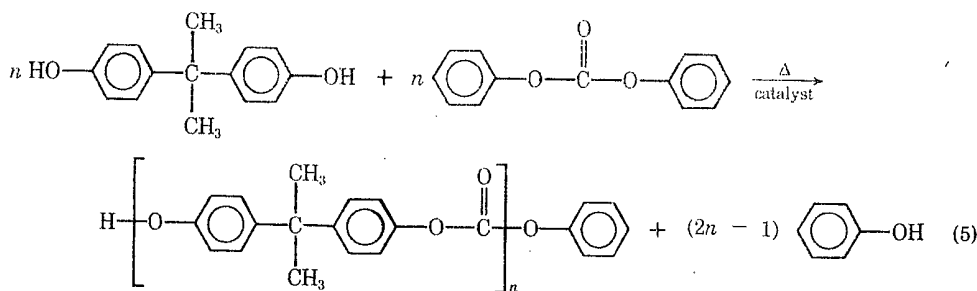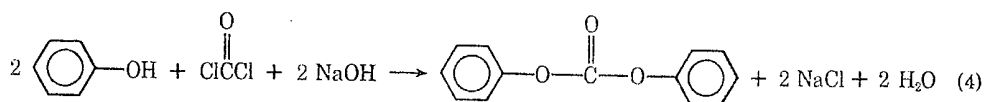
The diphenyl carbonate is prepared by passing phosgene directly into an aqueous caustic solution of phenol. Alternatively, it may be prepared in a two-phase reaction medium as employed in the direct interfacial procedure for polymerization (25). The crude diphenyl carbonate is purified by extraction with dilute base to hydrolyze and remove residual phenyl chloroformates, followed by distillation.

The polymerization may be conducted conveniently in two stages, prepolymerization and postpolymerization (26). Equal weights of bisphenol A and diphenyl carbonate (ca 6% excess) are melted together with 0.01–0.001 mol % basic catalyst, eg, $(\text{Na,K,Li})_2\text{CO}_3$ or calcium acetate, under a nitrogen blanket in a metal-clad resin kettle. Glass or glassed steel reactors are delaminated by the cooling polymer as a consequence of excellent adhesion of high molecular weight polymer to glass and very strong shrinkage forces.

The temperature of the melt should be raised until rapid distillation of phenol begins (200–225°C); then the temperature is gradually raised to 250°C at a rate that expedites phenol removal. A nitrogen sweep maintains an inert atmosphere and aids in the removal of phenol, which may be promoted also by a reduction in pressure. Approximately 60–70% of the theoretical amount of phenol may be removed conveniently before stirring becomes difficult. At this stage, the polymer has an intrinsic viscosity of 0.1 to 0.2 dL/g (as measured in chloroform at 40°C) depending on the amount of phenol removed.

The prepolymer may be ... ... intrinsic viscosities of ... ... vented extruders appear to be a solution. All ... ... during heat-

and mass transfer through a very viscous medium by promoting the generation of extensive surface. Since heat and mass transfer are rate-controlling, the time required for building molecular weight (as measured by intrinsic viscosity) from 0.20 to 0.55 dL/g can vary from minutes to hours, depending on the efficiency of the reactor system. The final high molecular weight polymer is recovered from the reactor by extrusion as strand or sheet, which may be chopped or diced to yield pellets for molding or further compounding.

Processing

The polycarbonates may be fabricated by all conventional thermoplastic processing operations, of which injection molding is the most common (see Plastics processing). Recommended operating conditions are stock temperatures of 275–325°C and molding pressures of 69–138 MPa (10,000–20,000 psi). Thorough predrying is required to prevent hydrolytic cleavage by entrapped moisture at the very high processing temperatures. Inadequate predrying may lead to surface-streaked parts and invariably loss of molecular weight. Typical properties of injection-molded parts are given in Table 1.

Extrusion produces film, sheet, and stock shapes. A polymer with a higher molecular weight than injection-molding grade is used. Temperatures vary between 285 and 315°C. Predrying also is important to this process.

Structural foam molding is a relatively recent development. The molding compound is charged with an inert gas under pressure and at the same time thermally plasticized in an extruder. Nitrogen gas may be pumped into the melt or the molding compound may contain a chemical blowing agent that decomposes with gas generation at the plasticizing temperature. The pressurized–plasticized melt is injected into a low pressure mold with a volume perhaps 25–30% larger than the compressed charge. The compressed gas in the melt causes the polymer to expand and fill the mold cavity. Very large parts with relatively low clamping pressures can be produced with this process, that is, structural parts with an expanded cross-section more resistant to deformation than a solid structure of the same weight. The surface is continuous, whereas the substrate is porous (see also Foamed plastics).

Injection blow molding of polycarbonates produces an assortment of containers from nonbreakable baby bottles to 20-L water bottles to outdoor-lighting protective globes. The polymer may contain a small percentage of polyfunctional monomer that acts as a branching agent (27). Introduction of slight branching has the effect of enhancing the melt strength.

Conventional thermoforming of sheet and film is applicable to the production of skylights, radomes, signs, curved windshields, short-run prototype production of body parts for electric cars, skimobiles, boats, etc.

Since bisphenol A polycarbonate is malleable, it can be cold-formed like metal and may be cold-rolled, stamped, or forged.

Economic Aspects

There is an official market for polycarbonate resins and there are a relatively few producers (see Table 2). According to a recent market-research publication, the 1982 world consumption of polycarbonates was 150,000 metric tons (29). The United States

Table 2.   Polycarbonate Manufacturers, 1980

	Product	Status
United States		
General Electric	Lexan	commercial
Mobay	Merlon	commercial
Dow		market sampling
Europe		
Bayer	Makrolon	commercial
General Electric	Lexan	commercial
Anic	Sinvet	commercial–Idemitsu Technology
ATO Chimie	Orgalan	importing from Mitsubishi Chemical
USSR		evaluating Anic Technology
Far East		
Teijin	Panlite	commercial
Mitsubishi Gas Chem.	Jupilon	commercial
Mitsubishi Chem.	Novarex	acquired Idemitsu production capability
Idemitsu	Taflon	no longer producing proprietary product
People's Republic of China		developmental polymer, possibly by transesterification

supposedly utilizes 50–55% of the total 75,000–83,000 t. A recent American publication estimates U.S. consumption at 109,000 t for 1980 (29). Future growth predictions vary from 8 to 12% per year. Construction, electrical–electronics, appliances, and transportation account for three fourths of the applications.

Health and Safety Factors

At least some base resins are produced in compliance with the conditions prescribed in Federal Food Additive Regulation 21CFR177.1580. Stabilizers, colorants, release agents, and antioxidants employed in molding compounds destined for food contact comply with appropriate regulations. Formulated compounds comply with extractive limitations set forth in Regulation 21CFR177.1580. Approvals of molded articles, where necessary, are the responsibility of the fabricator.

The toxicity of combustion products of plastic and wood construction materials has been rated (30). Unmodified polycarbonate was ranked 27th out of 30 (1 worst, 30 best) with respect to incapacitation and 30th with respect to lethality. No unusually toxic by-products were detected. The worst combustion component was carbon monoxide.

Uses

Extreme toughness, transparency, resistance to burning, and maintenance of useful engineering properties over a temperature range from −200 to +190°C are the outstanding features of polycarbonates.

insulation and mechanical housings for appliances; steam-sterilizable food-processing equipment; computer housings where mechanical, electrical, and fire-resistance properties are needed; safety helmets, ski mobiles, hockey gear, motorcycle shields, etc; automotive applications for light, impact-resistant bumpers and instrument panels; and solar collectors, storm windows, and skylights (see also Polyesters).

Production and applications for the standard commercial polycarbonate should grow even faster as patents run out and additional producers enter the field. Beyond the existing materials, many other opportunities remain to be explored.

OTHER POLYCARBONATES AND RELATED TECHNOLOGY

In the early commercial period, there was a broad and intensive search for new and more exotic polymers in the polycarbonate family (31). Some of the many bisphenols and polymers that were investigated are listed in Table 3. None of the homopolymers have been commercialized. The balance of properties obtainable from any of these polymers is not sufficiently attractive to justify the large investment for the commercialization of a new monomer and new polymer.

Copolycarbonates based on bisphenol A and tetrabromobisphenol A were more attractive. The bromine content enhanced the inherent fire resistance of the bisphenol A polymer to yield products with excellent ratings (15). Furthermore, brominated bisphenol A did not detract significantly from the excellent balance of properties of the basic polymer. Polycarbonates from tetrachlorobisphenol A were explored but not commercialized, partly because the pure monomer was too expensive.

Polycarbonates and copolycarbonates derived from 2,2-bis(4-hydroxyphenyl)-1,1-dichloroethylene have impact strength equivalent to that of bisphenol A polycarbonate, high transparency, outstanding resistance to burning, very low smoke from forced combustion, and low toxicity of combustion products (34–35).

A new polycarbonate is derived from tetramethylbisphenol A (33). Its monomer is produced by condensing acetone with 2,6-dimethylphenol, which is the monomer for General Electric's poly(2,6-dimethyl-1,4-phenyleneoxy) polymers (36). The polycarbonate [38797-88-5] from tetramethylbisphenol A resembles the dimethylphenylene ether polymers in their unusually high T_g value; ie, 207°C for the polycarbonate and 215°C for the polyether. Both polymers have excellent hydrolytic stability, one because it is a polyether and the other because of steric hindrance to hydrolytic action. The polycarbonate, like the polyether, is reported to be compatible with polystyrene. Under the assumption that the thermal oxidative stabilities are similar, the polymer will most probably be used in blend applications.

Polyester carbonates are produced by the reaction of diacid chlorides or diacids, phosgene, and bisphenols in the presence of an acid acceptor (37–38). When diacids are employed, phosgene first converts the carboxylic acids to the chlorides in situ, followed by reaction with the bisphenol. These combinations are of particular interest for high heat applications with incorporation of iso- and terephthalic acids.

These new polymers are characterized by relatively high heat distortion temperature transparent products than could be obtained with very high T_g based on combinations that were developed (40) (see Elastomers, synthetic).

Routes to carbonates and polycarbonates without phosgene are currently the

Table 3. Phenolic Polycarbonate Precursors
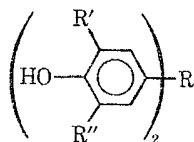
Substituent	Monomer CAS Registry Number	Mp, °C	Polymer Melt range, °C	T_g, °C	Ref.
R(R′ = R″ = H)					
$\diagup$CH₂	[620-92-8]	162–163	300		6
$\diagup$CHCH₃	[2081-08-5]	122	185–195	130	6
$\diagup$CH(CH₂)₃CH₃	[17181-62-3]		150–170	123	6
$\diagup$CHCH₂CH(CH₃)₂	[2081-32-5]		170–180	149	6
$\diagup$C(CH₃)₂	[80-05-7]	157	215–230	149	6
$\diagup$C(CH₂)₂CH₃ with CH₃	[77-40-7]	125	200–220	134	6
$\diagup$C(CH₂)₃CH₃ with CH₃	[4204-58-4]	149	200–220	137	6
$\diagup$CCH(CH₂)₂CH₃ with CH₃, CH₃	[14007-30-8]		180–200		32
$\diagup$C—CH(CH₂)₂CH₃ with CH₃, CH₃	[6807-18-7]	154–155	200–220	129	6
$\diagup$C(CH₂)₆CH₃ with CH₃	[1571-75-1]	68	170–190		6
$\diagup$CHCH₂C₆H₅	[6807-17-6]	175	210–230	176	6
$\diagup$CCHCH₃ with CHCH₃	[3600-64-4]	206–208	175–195	149	9
$\diagup$CCH(CH₃)₂CH₃ with (CH₃)₄CH₃	[7425-79-8]	155–157	175–200	143	32
$\diagup$C₆H₅·Pr	[79568-32-2]	150–151	240–250	192	

Table 3 (continued)

Substituent	Monomer CAS Registry Number	Mp, °C	Polymer Melt range, °C	T_g, °C	Ref.
>S==O	[1774-34-1]	203	230–250		32
—S(O)—O—	[80-09-1]	247–248	200–210		32
R(R′ = CH₃, R″ = H) >CH(CH₃)₂	[79-97-0]	137	150–170	95	32
R(R′ = R″ = Cl) >CH(CH₃)₂	[79-95-8]	133	250–260	180	32
R(R′ = R″ = Br) >CH(CH₃)₂	[79-94-7]	178–180	240–260	157	32
R(R′ = R″ = CH₃) >CH(CH₃)₂	[5613-46-7]	165		207	33
—S(O)—O—	[13288-70-5]	302	>300	250	45

subject of extensive research. Recently, aliphatic polycarbonates have been made by the organometallic-catalyzed reaction of carbon dioxide with epoxides (41). However, the reaction of carbon oxides with bisphenols to yield aromatic polycarbonates has not been reported. Therefore, attention has been focused on routes to diarylcarbonates without phosgene that could be employed in the transesterification process.

Many recent patents contain claims for the production of dialkyl carbonates by the catalyzed reaction of alcohols and carbon monoxide (42). Some claims and disclosures have been made for the conversion of dialkyl carbonates to diaryl carbonates (43). The direct production of diphenyl carbonate from phenol and carbon monoxide has been described (44). None of the disclosed chemistry appears to be sufficiently advanced to be considered as an alternative route to aromatic polycarbonates.

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D. W. Fox
General Electric Company

09/980010

「Refractive index control of transparent polymer」
"Chemical Survey" No.39, 1998, p174·175 edited by the
Japanese Chemical Society

(P174, lines 10 to 15)

At the beginning of the 1940 years, allyldiglycol·
carbonate (ADC, trade article name: CR·39) was
developed by the PPG in U.S.A. Regarding the ADC resin,
generally, ADC monomer was polymerized slowly over
many hours in the presence of 3% content of isopropyl·
percarbonate catalyst in a mold combined a glass mold
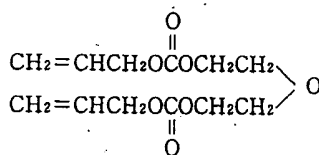and a resin gasket and molded (cast molding process).

$$CH_2=CHCH_2OCOCH_2CH_2 \diagdown O \diagup CH_2=CHCH_2OCOCH_2CH_2$$

Figure 1   allyldiglycolcarbonate

(P175, Table 1)

Table 1 main ophthalmic lens materials

Name of material	Refractive Index	Abbes's number	specific gravity
Glass			
Crown glass	1.523	59	2.54
High refractive	1.60	42.5	2.58
Index glass	1.70	40	2.99
	1.81	33	3.47
Plastic lens			
PMMA	1.49	58	1.19
ADC resin	1.50	58	1.32
DAP resin	1.55	40	1.27
PC	1.58	30	1.20
MR-6	1.60	36	1.35
EYAS	1.60	42	1.32
MR-7	1.66	32	1.35

PMMA:polymethylmetacrylate

ADC:allyldiglycolcarbonate

DAP:diallylphthalate

PC:polycarbonate

MR-6:trade article name, produced by Mitsui Toatsu
    Co., Ltd.

MR-7: trade article name, produced by Mitsui
    Toatsu Co.,Ltd.

EYAS:trade article name, produced by HOYA Co.,
    Ltd.

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